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DESCRIPTIVE GENERAL CHEMISTRY

A TEXT BOOK FOR SHORT COURSE

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PREFACE.



This book has been prepared to meet the requirements of the very short course in General Chemistry taught to the Cadets of the Military Academy.

The matter embraced is the result of more than sixty years' selection and sifting made in the effort to secure that most essential and important for this course. The arrangement adopted is that which long experience and careful consideration have shown to accomplish the best results in the time available for the study of the subject.

S. E. TILLMAN.

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ESSENTIAL PRINCIPLES OF CHEMISTRY.

The science of chemistry has for its object the study of the nature and properties of all kinds of matter and endeavors to classify the changes which matter undergoes. Nearly all substances accessible to man are of a compound nature, and may be decomposed or separated into simpler forms of matter, these simpler forms being generally very different from the original substances—thus, water is a compound substance and may be separated into its constituents which are gaseous bodies, oxygen and hydrogen. Common salt is a compound, one of its constituents being a white solid and the other a yellowish colored gas.

Those substances which thus far have not been separated into simpler forms of matter are called *elementary substances* or simply *elements*. The terms *chemical affinity*, *chemical attraction* and *force of affinity*, have been used to designate that force by virtue of which substances enter into combinations and form compounds. The compounds which are formed under the influence of affinity generally have properties entirely different from those of their constituents.

The force of affinity must be clearly distinguished from other forces exerted between all descriptions of matter, such as cohesion, which binds together the individual particles of the same body, and adhesion which designates the attraction existing between the particles of different bodies, as the adhesion of a liquid to glass; other effects are also observed which come under the head of molecular actions. From all these, chemical attraction is distinguished by the complete

change of character which follows its action; it might be defined as that property of matter by virtue of which new bodies are generated. This property of matter is concerned in all chemical changes, and chemistry may be defined as the science *which investigates the relations which affinity establishes between bodies, determines the laws governing its action, and examines the character and constitution of the substances which result from its operation.* Chemical changes permanently affect the properties of bodies, and physical do not.

There are at present recognized seventy-two elementary bodies but only sixty-two of this number have been obtained in the free state. The existence of the others is established from spectroscopic indications and from an examination of their compounds. Of the total number fifty-six are usually classed as *metallic* and the others as *non-metallic*. This division is in part arbitrary since the divisions graduate into each other. The accompanying table classifies the elements as above stated, the most important being distinguished by **heavier type** and *italics*.

These substances present every variety of physical character, state of aggregation, etc., some are solid, some liquid and some gaseous; some are light, others heavy, some occur in the free state and others only in combination. About sixteen elements make up ninety-nine hundredths of all known matter.

Table of Elementary Bodies, with Their Symbols and Atomic Weights.

Metals, Isolated.					
NAME.	SYMBOL.	ATOMIC WEIGHT.	NAME.	SYMBOL.	ATOMIC WEIGHT.
<i>Aluminium</i> ,	Al.	27.0	Magnesium,	Mg.	24.0
Antimony,*	Sb.	120.0	<i>Manganese</i> ,	Mn.	54.0
Barium,	Ba.	137.4	Mercury ,	Hg.	200.0
Bismuth,*	Bi.	208.9	Molybdenum,	Mo.	95.5
Cadmium,	Cd.	112.0	Nickel,	Ni.	58.0
Cæsium,	Cs.	132.6	Osmium,	Os.	198.5
Calcium ,	Ca.	40.0	Palladium,	Pd.	105.7
Cerium,	Ce.	140.4	<i>Platinum</i> ,	Pt.	194.4
Chromium,	Cr.	52.0	Potassium ,	K.	39.1
Cobalt,	Co.	58.9	Rhodium,	Rh.	104.0
Columbium (or Niobium),	Cb.	93.8	Rubidium,	Rb.	85.3
<i>Copper</i> ,	Cu.	63.2	Ruthenium,	Ru.	104.2
Didymium,	Di.	145.4	Silver ,	Ag.	108.0
Gallium,	Ga.	70.0	Sodium ,	Na.	23.0
Glucium (or Beryllium),	Gl.	9.0	Strontium,	Sr.	87.4
Gold,	Au.	196.2	Thallium,	Tl.	203.7
Indium,	In.	113.4	Thorium,	Th.	233.4
Iridium,	Ir.	192.7	<i>Tin</i> ,	Sn.	117.7
Iron ,	Fe.	56.0	Titanium,	Ti.	48.0
Lanthanum,	La.	138.5	Tungsten,	W.	183.6
Lead ,	Pb.	206.9	Uranium,	U.	239.8
Lithium,	Li.	7.0	Vanadium,	V.	51.3
			Zinc ,	Zn.	65.0
			Zirconium,	Zr.	89.4

Metals, not Isolated.

Decipium,	Dp.	159.0	Tantalum,†	Ta.	182.0
Erbium,	E.	166.0	Terbium,	Tr.	148.8
Holmium,	Ho.	162.0	Thulium,	—	170.4
Samarium,	Sm.	150.0	Ytterbium,	Yb.	89.1
Scandium,	Sc.	44.0	Yttrium,	Y.	172.8

Non-Metals.

Argon,	—	40.0	<i>Iodine</i> ,	I.	126.6
Arsenic,	As.	75.0	Nitrogen ,	N.	14.0
Boron,	B.	10.9	Oxygen ,	O.	16.0
<i>Bromine</i> ,	Br.	79.8	<i>Phosphorus</i> ,	P.	31.0
Carbon ,	C.	12.0	Selenium,	Se.	78.8
Chlorine ,	Cl.	35.5	<i>Silicon</i> ,	Si.	28.2
<i>Fluorine</i> ,	F.	19.0	Sulphur ,	S.	32.0
Hydrogen ,	H.	1.0	Tellurium,	Te.	128.0

*Because of their chemical properties Antimony and Bismuth might with propriety be classed as non-metals.

†The existence of this body is beyond doubt, but its *certain* isolation has not been accomplished, though it is sometimes classed with the isolated metals.

LAW OF FIXED OR DEFINITE PROPORTIONS.

The relative weights of the constituent elements in any chemical compound are fixed—or, the same compound always contains the same elements in the same proportions by weight. This was the first general law governing chemical action discovered; it was recognized before but not fully established until the beginning of this century. Thus in 100 pounds of water, which is a compound of oxygen and hydrogen, there are always

88.889 pounds of oxygen
and 11.111 pounds of hydrogen.

In 100 grains of lime which is a compound of calcium and oxygen there are always

28.571 grains of oxygen
and 71.429 grains of calcium.

The same fixity of proportions exists among the constituents of all compounds.

It is the law of definite proportions which so clearly distinguishes true chemical compounds from mere mechanical mixtures; in the first the constituents are always in fixed proportions, in the mixture they may be in any proportions; in a mixture the ingredients may generally be distinguished and separated by mechanical means alone, but such means are not alone sufficient to distinguish or separate the constituents of a chemical compound. Again, as has been stated, in a chemical compound the properties of the constituents have entirely disappeared, but in a mixture the properties of the ingredients exist in varying degrees depending upon the proportions of the ingredients themselves.

SOLUTIONS AND ALLOYS.

Although these distinctions characterize true chemical compounds and mechanical mixtures there are classes of bodies such as solutions and alloys in which these distinctions do not so plainly exist. Bodies in these states appear

to be in less intimate condition than true chemical union and more so than that of mechanical mixture. These bodies (solutions, alloys, etc.) graduate imperceptibly on the one hand into true chemical compounds and on the other into mere mixtures. The law governing the formation of such bodies is not known. The word *compound* in the text is always used to indicate a true chemical compound—that is, one in which the proportions of the constituents are invariable and otherwise characterized as above stated.

LAW OF MULTIPLES.

The same elements generally unite in more than one proportion forming different compounds, in such cases the proportions of the elements produce simple ratios; the law may be more specifically stated as follows: *when two bodies, A and B unite in several proportions the different quantities of B which unite with a fixed quantity of A bear a simple ratio to each other*, thus the several quantities of sulphur which unite with the same quantity of potassium are to each other as the numbers 1, 2, 3, 4 and 5 and the same numbers give the different amounts of oxygen which unite with the same quantity of nitrogen, as illustrated in the following tables:

POTASSIUM.	SULPHUR.	NITROGEN.	OXYGEN.
2.438	1	1.75	1.
2.438	2	1.75	2.
2.438	3	1.75	3.
2.438	4	1.75	4.
2.438	5	1.75	5.

This is the second general law governing chemical action that was established.

THE ATOMIC THEORY.

The above law was discovered by Dalton of Manchester, and his writings show that he had observed it as early as 1802. From his investigations during 1803 and 1804 he

gained a clear conception of the law and it is involved in the results at which he arrived, though it was not published until 1805.

At about the same time, and largely by the consideration of the same data that established the Law of Multiples, Dalton was led to propose the Atomic Theory, which was first published in 1807. This theory, as conceived by Dalton, asserts that all simple bodies are composed of small indivisible particles, or atoms, the atoms of any element having all the same weight, which is different from the weight of the atoms of all other elements, and chemical compounds result from the combination of atoms of different substances.

The law of definite proportions and the law that the quantities of one element which can unite with a constant quantity of another increase successively by well defined steps and not continuously, or the law of multiples, are both reasonably explained by this theory; in the first case it is only necessary to conceive that the substance always contains the same number of atoms of each of its elements, in the second case more than one compound between two elements can result only by the successive additions of one or more entire atoms. The weight of the particle of the new body formed by the union of atoms was by Dalton held to be equal to the sum of the weights of the atoms entering it.

The above is the substance of Dalton's Atomic Theory. In its essential points it has been strengthened by the subsequent test of experimental research and in its expanded form is the basis of the developed chemistry of to-day. The atoms in Dalton's theory were assumed to be indivisible, but the chemistry of to-day merely asserts that they have not been divided and not that they cannot be.

The particles of matter resulting from the combination of the same or different kinds of atoms are now termed *molecules*. The same kind of atoms combining form a molecule of an elementary substance, while different kinds form

a molecule of a compound substance. The chemical conception of molecules is thus clear and defined:

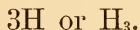
The molecule is the smallest mass of the substance which retains all and only the qualities of the substance itself.

The body is but an aggregate of molecules, each of which has properties identical with those of the body itself. If the molecule of a compound substance be resolved into its constituents the properties of the compound are destroyed.

The atoms are the smallest individual masses yet known to enter the molecules. They do not ordinarily exist separately, but are combined with the same or different kinds of atoms, forming, in the first case, elementary and, in the second, compound molecules; compound molecules themselves sometimes unite forming molecules of still greater complexity, or molecules of the second order, or even higher orders.

CHEMICAL NOTATION.

Elements. The atomic theory is expressed in the notation employed in chemistry. The symbols of the elements are given in the second column of the preceding table. The symbols employed are the first letters of the Latin names of the elements, a second letter being added when the names of more than one element begin with the same letter. These symbols represent atoms of their respective elements, the different atoms of different substances having different weights as already stated. Several atoms of the same element are represented by placing a coefficient before the symbol or a numeral to the right and below, thus three atoms of hydrogen are represented by



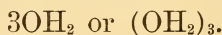
Compounds. A molecule resulting from the combination of atoms of different kinds is represented by placing the symbols of the atoms in juxtaposition, thus, a molecule of common salt, a compound of sodium and chlorine, is represented by



If more than one atom of either element enters the molecule it is shown by placing the corresponding numeral to the right and below the symbol of the element, thus a molecule of water is a compound of one atom of oxygen and two of hydrogen and is represented by



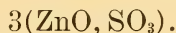
When it is desired to indicate several molecules the numeral is placed as a coefficient or the molecule is enclosed in brackets and the numeral placed to the right, thus, three molecules of water would be represented by,



A combination of molecules is sometimes indicated by their juxtaposition with a comma between, thus the combination of zinc oxide (ZnO) and sulphuric oxide (SO_3) is indicated by



to indicate a group of such molecules they are enclosed in brackets and a coefficient placed to the left, thus



Combinations of molecules, however, are more generally indicated by grouping the symbols of the elements involved and placing the proper numerals to the right and below to show the number of *atoms* of each element which enter; thus the compound above would be written



A molecule of water (OH_2) combining with a molecule of sulphuric oxide (SO_3) would form a molecule represented by



Again, CO_2 combining with OH_2 would give



These molecules are multiplied by placing a coefficient in front as,



NOMENCLATURE.

The names of the elements correspond to no fixed rule, Some are named in allusion to a certain property, or to a circumstance connected with their discovery or history. The names of the more recently discovered metals end in *um* and several of the more recent non-metals in *ine*, as sodium, potassium, platinum; chlorine, bromine, etc.

Binary Compounds. Compounds are termed binary, ternary, quaternary, etc., according as they contain two, three or four elements. Binary compounds of metallic and non-metallic elements are usually named by changing the termination of the non-metallic element into *ide*—thus, compounds of oxygen, chlorine, sulphur, etc., with metals are called respectively oxides, chlorides, sulphides, etc., as potassium oxide, sodium chloride, lead sulphide, etc. The same method of naming holds in binary compounds of non-metallic elements; the termination of the more distinctly non-metallic element is changed into *ide*, thus a combination of S and O forms a sulphur oxide, of H and Cl a hydrogen chloride, of C and O a carbon oxide, etc.

Oxides. The oxides are very numerous and important and for convenience are divided into two principal classes. The first class contains all those oxides whose chemical properties are similar to those of the oxides of K, Na, Pb, etc., and are called basic oxides. The second class contains all those oxides whose chemical properties are similar to the oxides of S, C, P and N, etc., and are called acid oxides; generally the oxides of the metals are basic and of the non-metals acid. Some of the acid and basic oxides are capable of uniting directly and forming compounds called *salts*, thus when the oxide of sulphur (SO_2) in vapor, is passed over heated barium oxide (BaO), combination ensues and a salt called barium sulphate (BaSO_4) is formed. There is also an intermediate group of oxides designated as *neutral oxides* because

of their slight disposition to enter into combination; manganese dioxide (MnO_2) is an example of this class. These neutral oxides may also be formed from non-metals; water (H_2O) and carbon monoxide (CO) are examples. These classes are not separated by distinct lines but graduate into each other; the same oxide may sometimes exhibit either acid or basic properties according to circumstances. Again, although the most characteristic basic oxides are oxides of the metals, yet some of the *higher* metallic oxides exhibit acid properties and some of the metals form only acid oxides.

Oxy-Acids. Most of the acid oxides unite readily with water forming compounds called oxy-acids, which possess to a marked degree the properties termed acid, such as sour taste, corrosive action, the power of reddening certain blue vegetable colors and yet more important, the power of exchanging the hydrogen which they contain for a metal and forming salts. Thus the oxide of sulphur (SO_3) called sulphuric oxide, unites energetically with water (OH_2) forming sulphuric acid, the formula for which is SO_4H_2 . Again the oxide of nitrogen (N_2O_5), called nitrogen pentoxide, will unite with water forming nitric acid ($\text{N}_2\text{O}_6\text{H}_2$) or $2\text{NO}_3\text{H}$. Carbon dioxide (CO_2) also unites with water forming (CO_3H_2) carbonic acid. Sulphuric or nitric acid will act upon zinc and exchange its hydrogen for the metal and form a salt called zinc sulphate or zinc nitrate. The property of exchanging their hydrogen for a metal is the most characteristic property of acids and will be referred to again. It is now seen that salts may be formed in two ways, either by the direct union of basic and acid oxides or by the replacement of the hydrogen in an acid by a metal.

Prefixes. Binary compounds of oxygen following the law of multiples are distinguished as *mono*, *di*, *tri*, *etc.*, according to the degree of oxidation, a compound intermediate between a monoxide and a dioxide is called a sesquioxide, as

CrO ,	chromium monoxide;
CrO_2 ,	chromium dioxide;
CrO_3 ,	chromium trioxide;
Cr_2O_3 ,	chromium sesquioxide; etc.

Binary compounds of the other elements under the same law are designated in the same way, as,

monosulphide,	monochloride,
disulphide,	dichloride,
etc.	etc.

Suffixes. When an element forms but two oxides they are also often distinguished by placing before the word *oxide* the name of the element with the termination *ous* for the lower, and *ic* for the higher oxide, thus

Sulphurous oxide, SO_2 .

Sulphuric oxide, SO_3 .

Carbon dioxide, CO_2 .

These same terminations are also used to specify the two more important oxides of an element even when it forms more than two oxides, thus, the basic salifiable (salt forming) oxides of iron are

FeO , ferrous oxide,

Fe_2O_3 , ferric oxide.

The salts which are formed from such oxides have the same terminations, as ferrous and ferric salts.

It has been stated that the acid oxides unite with water, forming oxy-acids, and that these acids may form compounds called salts, by exchanging their hydrogen for a metal. If the *name* of the oxide terminates in *ous* the name of the acid formed by its union with water also terminates in *ous*, thus

Sulphurous oxide unites with water and forms sulphurous acid;

Nitrous oxide unites with water and forms nitrous acid;

Phosphorous oxide unites with water and forms phosphorous acid.

The salts which result from these acids by exchanging their hydrogen for a metal, have the termination *ite*—thus, salts from sulphurous acid are called *sulphites*, from nitrous acid, *nitrites*; as, lead sulphite, potassium nitrite, etc. If the oxide terminates in *ic* the acid formed by its union with water has the same termination—thus

Sulphuric oxide unites with water, forming sulphuric acid;

Nitric oxide unites with water, forming nitric acid;

Phosphoric oxide unites with water, forming phosphoric acid;

Carbon dioxide unites with water, forming carbonic acid, etc., etc.

The salts which result from the oxy-acids ending in *ic*, by an exchange of hydrogen for a metal, have the termination *ate*, thus salts from the last named acids are sulphates, nitrates, phosphates, respectively—as lead sulphate, potassium nitrate, etc.

In naming binary compounds, the Latin prefixes uni, bi, ter, etc., are sometimes used instead of the Greek, but the latter are more generally employed.

Hydracids. The acids above referred to are all oxy-acids and it was once supposed that all acids contained oxygen. We now know that there are bodies possessing all the properties of acids which do not contain oxygen, they all, however, contain hydrogen and they are capable of exchanging this hydrogen for a metal and forming salts. Some of the acids which contain no oxygen are composed of hydrogen and one other element. There are only a few such examples, some of them are—*hydrochloric acid* (HCl), *hydrobromic acid* (HBr), *hydrofluoric acid* (HF), *sulphydric acid* (SH_2). The salts formed by replacing the hydrogen in the hydracids by a metal are named in accordance with the rule for binary compounds. Thus, when the hydrogen in hydrochloric acid is replaced by zinc, we have zinc chloride

—if potassium replace the hydrogen, in hydrobromic acid, we have potassium bromide, etc.

The above system of nomenclature is the one most generally followed, but there are slight departures from it by certain chemists. The principle of the system is that the composition of the compound shall be briefly expressed in its name. In addition to this, many substances have popular names which will be found in the text, or have been otherwise named as will be subsequently explained.

CHEMICAL REACTIONS.

Nearly all chemical changes result from the reciprocal action of chemical agents upon each other and are therefore called *reactions*. Those substances which differ most in chemical properties act most readily upon each other. From the definition of molecules it is evident that these changes take place among the molecules, and although these molecules are invisible it should be appreciated that whatever chemical changes occur in the bodies must come through an alteration of their molecules. By means of the symbols given we can represent the changes which occur. Reactions are usually represented by equations, in the first member of which are placed the symbols of the substances employed called *reagents*, and in the second member the symbols of the products obtained. Reactions consist either in the direct addition or separation of elements, or in the substitution of an atom of one element for one or more atoms of another element, or of a group of atoms of one molecule for a similar group of another.

We thus have *first*, *synthetical* reactions in which a more complex body is formed by the union of simpler bodies; in this case the bodies should be opposed in properties. Thus—

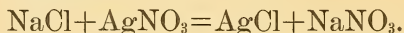


Second, analytical reactions, as when calcium carbonate is heated it yields calcium oxide and carbon dioxide, thus—



In this class a more complex body is broken into simpler ones.

Third, metathetical reactions, in which the transformation of previously existing compounds is brought about either by simple substitution or double decomposition, thus—



In the case of double decomposition, if the body desired be a salt, one of the reagents must contain the acid part and the other the basic part of the salt desired.

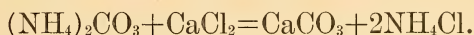
These equations are but the expressions of observed facts, and their truth is known from observation, and not from deduction. They express only the known results from known premises and give no indication of the complex phenomenon of the reaction itself. They represent the distribution of weights before and after chemical change. In every reaction, since there is only a change, and not a loss or destruction of matter, the total weights of matter in the two members must be the same, as also must be the total number of atoms of each and all the elements. Some substances occur native, but the majority of them are obtained by one or the other of the above methods. The most common reactions are of the metathetical kind.

Affinity has been defined as a property of matter by which new compounds are formed. It is frequently conceived to be the *cause* of chemical action and hence termed the *force* of affinity. It is essentially concerned with action between atoms but also extends to action between molecules. Without limiting the conception of affinity it is convenient to adhere to the practice of designating it as a *force*. There are conditions and circumstances under which reactions

occur more readily than others and the force of affinity may be said to vary with conditions, and except under entirely known conditions it is entirely impossible to predict the result of an experiment. As illustrating the above statements we may refer to certain adventitious circumstances which influence chemical actions or their results.

CONDITIONS AFFECTING AFFINITY.

Insolubility. It is a rule almost without exception that *when two soluble salts, containing the constituents of an insoluble, or sparingly soluble one, are brought together in solution the salts decompose each other and the less soluble salt is formed.* This rule may be illustrated by bringing together in solution ammonium carbonate and calcium chloride, when the calcium carbonate will be formed and precipitated, as indicated by the reaction:



Volatility. In many instances *when two salts, containing the constituents of a volatile one, are heated together the volatile one is produced and driven off.* This is illustrated when calcium carbonate and ammonium chloride are heated together, ammonium carbonate is formed and volatilized.



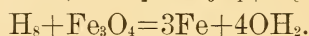
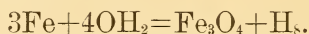
Again, certain acids or acid oxides which are volatile may be displaced by others of feeble attraction, but which are not volatile.

Solution. The force of affinity acts only at insensible distances and whatever tends to prevent the closest proximity of the molecules tends to prevent action. Owing to cohesion in solids and the distance between the particles in the gaseous state, neither of these is most favorable to chemical action. In solution cohesion is slight, and the distance between particles is small, and this is the most favorable state for chemical action, consequently it is often

desirable to bring one or both of the bodies to a state of solution.

Of the other causes which affect the force of affinity we may mention *Temperature*, for at one temperature mercury unites with oxygen, and at a different temperature the oxygen separates from it.

Physical Surroundings. If the vapor of water be passed over heated iron filings it is decomposed and iron oxide is formed; on the other hand, if hydrogen gas be passed over heated iron oxide it reduces it to the metallic state, while the vapor of water is reformed.



Again, if sulphydric acid gas in excess be passed over acid potassium carbonate, slightly heated, carbon dioxide is liberated and potassium sulphide formed, whereas, if carbon dioxide be passed through a solution of potassium sulphide the acid carbonate is reformed and sulphydric acid gas passes off.

The nascent state is one very favorable to chemical action; this is the condition in which bodies exist when just liberated from some combination. Thus, if free hydrogen be passed into nitric acid there is no action, but if the acid act upon zinc immersed in it the hydrogen set free decomposes a portion of the acid.

Catalytic Action. This refers to effects which are apparently brought about by the mere presence of a body. Thus, if potassium chlorate be heated with manganese dioxide it is decomposed more easily than when heated alone. The same effect is produced by the presence of other oxides, and is probably due to the fact that these oxides pass to a state of higher oxidation and then in turn are themselves reduced. Only oxides capable of higher oxidation produce the result.

Disposing Affinity. This term is used to embrace an extensive class of actions which are induced by the presence of certain bodies and which would not occur in their absence. It differs from the catalytic action in that the disposing body is found to be changed at the close of the operation, while the influencing body in catalysis is not.

It should be understood that these so-called cases of modified chemical action are only the statements of facts invariably observed. These facts will soon undoubtedly be included under the more perfectly developed laws governing chemical action. Many examples of this action will be observed as progress is made in the course.

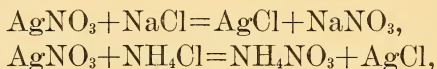
Influence of Pressure on Chemical Action. When a body is decomposed, in a confined space, by heat, some of the products being gaseous, the decomposition will go on until the liberated gas or vapor has attained a certain pressure, greater or less according to the temperature. No further decomposition will then take place nor will the elements or constituent gases recombine so long as the temperature remains fixed; but if the temperature be raised the decomposition will begin again and continue until the vapor reaches a tension definite for that temperature, when it will again cease; if on the other hand, the temperature is lowered, recombination ensues until the tension of the remaining gases is reduced to that corresponding to the lower temperature. Decomposition under these conditions has been designated by Deville by the term "Dissociation."

The effect of pressure is also seen in the retarding influence it exerts in the action of acids upon zinc. If the escape of the gas which is liberated is prevented the action is retarded. On the other hand, there are numerous reactions which are greatly promoted by increased pressure, such as those which depend on the solution of gases in liquids, or on the prolonged contact of substances which under ordinary circumstances would be volatilized by heat.

RADICALS, BASES, ACIDS, AND SALTS.

We are now prepared to supplement the system of nomenclature given, to a certain extent, and to explain the use of certain terms which have long been, and still are in use in chemistry, and to more fully define others which we have already used.

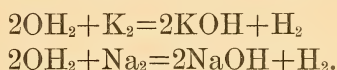
Radicals. In the metathetical reactions it was indicated that the elementary atoms not only change places with each other, atom for atom, but one atom with more than one of another kind, or one with a group of other kinds or groups of atoms of different kinds with each other. These interchanging atoms or groups appear to bear the same relations to the molecules they enter as did the atom or atoms replaced. Thus, in the following reactions—



the atom of silver is replaced in the first by an atom of sodium, in the second by the group (NH_4). Such groups of atoms are called *compound radicals*, and it is assumed that in ordinary reactions they are transferred from molecule to molecule without loss of integrity. The elementary atoms which perform similar parts in different molecules may be called *elementary radicals*, so that the term radical is applicable to both elementary atoms and groups of atoms. Only a few of the compound radicals have been isolated. They are assumed to so exist because the same group, or, at least the same proportional amounts of the same elements enter several compounds. The symbol of every compound molecule may be formulated into possible radicals, but unless the radicals enter several compounds there is nothing gained by the assumption. Radicals are designated as *acid* or *basic* according as they fulfill the parts of *acid* or *basic* compounds. Of elementary radicals, generally the metallic atoms are basic, and the non-metallic atoms acid radicals. Thus, in

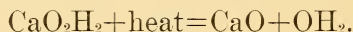
NaCl the sodium is the basic and the chlorine the acid radical. In ternary combinations the compounds of oxygen with the metals are usually basic radicals and the compounds of oxygen with the non-metals acid radicals. Thus, in $3K_2O$, As_2O_5 , the molecule K_2O is basic, the other the acid radical; in Na_2SO_4 the Na_2 is the basic, and the SO_4 the acid radical. Compound radicals consisting of carbon and hydrogen only, are usually basic, but those which contain oxygen also, are generally acid. The radical NH_4 is strongly basic. The basic radicals are also called *electro-positive*, and the acid *electro-negative* radicals.

Bases. This term is more general than *basic oxide* (already-mentioned) and includes a class of bodies designated *basic hydrates*, simply *hydrates* or better *hydroxides*. These hydrates were formerly supposed to contain water as such, but now they are believed to contain oxygen and hydrogen in the form of hydroxyl (OH) and not in the form of water (OH_2). They can usually be formed from water by replacing half its hydrogen by a metallic *element*. Thus,

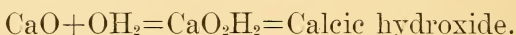


These hydroxides of potassium and sodium and also those of lithium, caesium and rubidium are very soluble in water and give solutions which corrode the skin and convert fats into soaps; they differ from the hydroxides of all other metals (except that of barium) in that they are not decomposable by heat alone. Very similar to them in chemical properties is the hydroxide of ammonium formed by dissolving ammonia gas (NH_3) in water. All of the hydroxides just named are called *alkalies*. The great similarity of ammonium hydroxide to the others named gives grounds for the assumption that the radical..... NH_4 exists, and that ammoniac hydroxide may be formulated, NH_4OH just as potassic hydroxide is KOH .

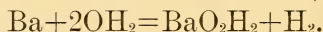
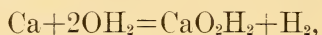
The hydroxides of Ba, Ca, Sr and Mg are called *alkaline earths*. They are less soluble than the alkalis, less caustic, and, except that of Ba, can be decomposed by heat into a metallic oxide and water. Thus,



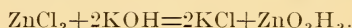
This process may be reversed, and the hydroxide obtained by mixing the metallic oxide with water. Thus,



The hydroxides of this group can also be obtained by replacing half the hydrogen in water by the metallic atom, thus—



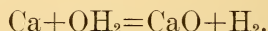
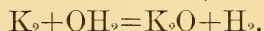
The hydroxides of many of the other metals are still more readily decomposed by heat, and can not as a rule be formed direct from the oxides and water. They may be obtained by adding a solution of a soluble salt of the metal to one of the hydrates named above. Thus,



The hydroxides may all be regarded as compounded of metallic atoms with the radical hydroxyl (OH). Thus,



Metallic Oxides, Basic Anhydrides. Just as hydroxides are obtained by replacing half the hydrogen in water by a metallic atom or basic radical, so the metallic oxides or basic anhydrides may be considered as formed by a replacement of all the hydrogen in one or more molecules of water by metallic atoms. Thus,

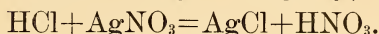
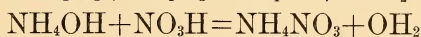
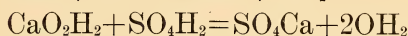
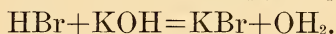
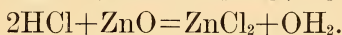
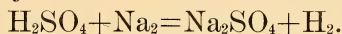


The term *base* in inorganic chemistry is generally applied to both hydrates and basic anhydrides and also to certain compound radicals, all of which form salts with acids, but there is a tendency to limit the term to *hydroxides*.

Acids. The general properties of acids have already been stated, the most characteristic of which is their capacity to

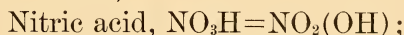
exchange a part or the whole of the hydrogen which they contain for metallic elements or basic radicals. Some of the acids contain only hydrogen and one other element, as hydrochloric acid (HCl), hydrobromic acid (HBr), sulphydric acid (SH_2), &c., but most acids consist of hydrogen and more than one other element, as H_2SO_4 , sulphuric acid; HNO_3 , nitric acid; CO_2H_2 , carbonic acid; &c.

The hydrogen in all these acids may be replaced in several ways—by acting on the acid with either a metal, metallic oxide, hydroxide or a metallic salt. Thus,



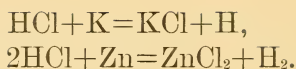
It is thus seen that although salts are sometimes formed by the direct union of a basic and an acid oxide (see page 13) they are far more generally formed by the replacement of the hydrogen in an acid, in part or whole, by a basic radical either elementary or compound.

The acids without oxygen are called hydrogen acids, or *hydracids*, and those containing it oxygen acids or *oxy-acids*. The oxygen acids like the hydrates may be regarded as compounds of hydroxyl with an acid radical instead of with a basic radical. Thus,



Basicity of Acids. When an acid contains but *one* atom of hydrogen in its molecule replaceable by a metal or basic radical it is said to be *monobasic*; when *two*, *bibasic*; when *three*, *tribasic*; &c.

Monobasic acids can form but one class of salts, the metal replacing the whole of the hydrogen in one or more molecules of the acid. Thus,



A bibasic acid may form two classes of salts, viz.:—*primary* or *acid* salts in which only half the hydrogen in the molecule is replaced, and *secondary* salts in which the whole is replaced; in the latter case if the hydrogen is replaced by one metal the salt is called *normal*, and if by two metals *double*. Thus,

KHSO_4 is an acid salt, acid potassium sulphate.

K_2SO_4 is a normal salt, normal “ “ .

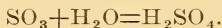
KNaSO_4 is a double salt, potassio-sodic “

Tribasic acids may form three classes of salts—primary, secondary or tertiary, including normal, double and triple, in which the hydrogen is wholly or partially replaced by one or more metals. The following list contains the most important and common inorganic acids, arranged according to basicity:

MONOBASIC ACIDS.		BIBASIC ACIDS		TRIBASIC ACIDS.
Hydrochloric,	HCl.	Hydric (water)	OH_2.	Orthophosphoric
Hydrobromic,	HBr.	Sulphydic,	SH_2.	H_3PO_4
Hydriodic,	HI.	Sulphuric,	SO_4H_2.	
Hydrofluoric,	HF.	Carbonic,	CO_3H_2.	
Nitrous,	HNO_2 .	Pyrosulphuric,	$\text{H}_2\text{S}_2\text{O}_7$.	
Nitric,	HNO_3.			
Chloric,	HClO_3 .			

Acid Anhydrides. The application of the term acid oxide has been already given (page 13). Many of these oxides can be obtained by abstracting the constituents of water from acids, and hence have also received the names of *acid anhydrides* or simply, *anhydrides*.

As has been stated, most of these anhydrides display great readiness to unite with water, forming acids. Thus,



In this respect they bear the same relation to acids that basic oxides do to hydrates.

Salts. The formation of salts by the direct union of acid and basic oxides, and by the replacement of the hydrogen in an acid, by different methods, have been already referred to. Now it is evident that, in the reaction between acids and hydroxides, while we considered that the hydrogen of the acid

was replaced by a metallic atom or basic radical, we might, with equal propriety, have considered the hydrogen of the hydrate as replaced by an acid radical, thus:



From these considerations it is evident that the term *salt* is a descriptive one and cannot be defined in independent language.

If only a part of the hydrogen in the hydroxide be replaced by the acid radical the salt is called *basic*. Basic salts are also defined as those formed by the union of a normal salt with a basic oxide or hydroxide, the base thus being in excess of that necessary to form a normal salt. On the other hand, a normal salt may combine with an acid oxide so that there is an excess of acid oxide over that necessary to form a normal salt: such a salt is called an *anhydro* salt.

EQUIVALENT WEIGHTS OR EQUIVALENTS.

It has already been stated that substances may replace each other in combination and that chemical actions generally consist of an interchange between the elements of different molecules. When HCl acts upon Zn, the zinc replaces the hydrogen, which is evolved as a gas; when potassium is thrown upon water it replaces the hydrogen of the water forming KOH; if mercury be added to a solution of silver nitrate the silver is replaced by the mercury and itself deposited.

The replacement of one element by another always takes place in fixed proportions. *The relative quantities of the elements which thus replace each other in combination are called equivalent weights or chemical equivalents.* Equivalent weights are those quantities of the elements which possess the same chemical value and are capable of filling each other's places directly or indirectly. *The chemical equivalents are made specific by defining them as those weights which will combine with or displace, or are chemically equivalent to, one part by weight of hydrogen.*

Strictly speaking, quantities of elements could only be said to be equivalent when they had actually replaced each other in combination, but quantities of elements which are equivalent to the same quantity of another element are assumed to be equivalent to each other, thus 35.5 parts of chlorine are known to unite with 1 part of hydrogen, 23 of sodium and 108 of silver, consequently the numbers 1, 23 and 108 are the equivalent weights of hydrogen, sodium and silver. In a similar way the equivalents of all elements may be expressed.

These equivalents are the result of direct experiment and are based on no hypothesis as regards the constitution of matter. But in addition to the fact that many of the equivalent weights have to be determined indirectly there is another difficulty which arises as soon as we consider those bodies which combine in more than one proportion, thus, tin forms two chlorides in one of which 58.5 parts of the metal are combined with 35.5 parts of chlorine and in the other 29.25 parts of tin are combined with the same amount of chlorine; which of these is to be taken as the equivalent weight of tin? The same difficulty is encountered in all cases in which combination occurs in more than one proportion between elements, and as most bodies combine in more than one proportion the idea of equivalent weights is not definite.

ATOMIC WEIGHTS.

The distinction between atoms and molecules has already been given and although the atom is the smallest mass of matter yet distinguished, the modern chemistry does not assert that the atom is beyond the limit of divisibility, it simply asserts that it has not yet been divided and that in all known chemical processes the atomic masses act as units, and it matters not what may yet be accomplished in dividing atoms, their integrity is retained in all reactions with which we are at present familiar.

With the promulgation of the atomic theory the determination of the relative weights of the elementary masses or the relative combining numbers became an absorbing problem. These weights are the numerical constants of the science of Chemistry—they are the essential data in all quantitative analysis as well as in the application of Chemistry to the necessities of daily life. To make possible a clear understanding of the method of determining atomic weights the student must bear in mind that although we cannot isolate and operate upon a single molecule of a body, yet in transforming a body we but transform its individual molecules and whatever change the body undergoes is also undergone by each molecule thereof and whatever relation is found to exist among the constituents of a body also exists among the constituents of a single molecule.

Determination of Atomic Weights by Analysis. By accurate analysis we can determine the proportions of the elements which enter many compounds and consequently the proportions of the elements which enter the molecules, and if we knew the number of atoms of each element in the molecule we could deduce the relative weights of the atoms.

Thus, the analysis of water shows that oxygen and hydrogen enter the molecule in the proportion by weight of oxygen=8 and hydrogen=1. If there were an equal number of atoms of each element in the molecule the numbers 8 and 1 would represent the atomic weights. Now there is another compound of oxygen and hydrogen in which the proportions by weight are oxygen=16 and hydrogen=1. Assuming from the first compound that the atomic weights are 8 and 1 we might in the second case conclude that the compound contained two atoms of oxygen; this would then account for the new proportion 16 to 1, but if we, with equal propriety, assume that the second compound contains one atom of each of the elements then the relative atomic weights are 16 and 1 and the first compound, water, necessarily contains two atoms of hydrogen.

Thus with nothing before us except the results of simple analysis, the atomic weights would be uncertain, they might be correct or they might be multiples or sub-multiples of the correct ones, depending upon whether or not the number of atoms which enter the molecule was correctly assumed.

Determination of Atomic Weights by Substitution. The method of substituting one element for another can often be made use of to assist in reaching a correct conclusion as to the number of atoms which enter the molecule.

For example, if water be treated with metallic sodium it is acted upon in such a way as to produce a substance whose composition is

Sodium,	Hydrogen,	Oxygen
23	1	16

and if this compound be evaporated to dryness and heated with more sodium the remaining portion of the hydrogen is driven out and replaced by the sodium and we have a compound of

Sodium,	Sodium and	Oxygen.
23	23	16

It is thus evident that the hydrogen in the molecule of water has been replaced by halves and it follows from the conception of atoms that there must have been at least two atoms in the molecule. Now if we could be certain that the molecule contained only one atom of oxygen we would again have the atomic weights of hydrogen and oxygen to be 1 and 16. With only the data yet before us we could not certainly conclude that the molecule of water has but one atom of oxygen and hence the atomic weights would still be uncertain.

Again, if we take marsh gas, a compound of carbon and hydrogen, the hydrogen may be replaced by four separate substitutions, so that there must be at least four atoms of hydrogen in the molecule of marsh gas and if it be assumed

that they are combined with one atom of carbon we arrive directly at the atomic weights. But as in the preceding case the number of atoms of each element is not determined by substitution alone and the atomic weights would remain uncertain.

Determination of Atomic Weights by Decomposition. By the decomposition of certain bodies and the formation of others it is sometimes possible to compare the amounts of a certain element in the two and if the number of atoms of the element in either be known the number in the other is also determined.

The above are the only purely chemical means for the determination of atomic weights and it is seen that they leave a doubt as to the correct numbers. It should be borne in mind that by a combination of all the methods and by an examination and comparison of various compounds of the same element the uncertainty is very small. Thus, in the case of carbon it is indisputable that the smallest increment or decrement which can be made in any compound is 12 times as great as the smallest weight of hydrogen that can be introduced or displaced and if we adhere to the smallest *separable* portion as the atom, the uncertainty as to the atomic weight is exceedingly slight in the case of this and many other elements.

These purely chemical methods for the determination of atomic weights have been supplemented by means dependent upon physical considerations. The coincidences between the results obtained by these different means are so satisfactory as to dispel doubt as to the correct atomic weights of the great majority of the elements except such doubt as is due to imperfection of process. We will now explain the method of determining the atomic weight by the introduction of physical considerations.

PHYSICAL AND CHEMICAL RELATION OF ATOMIC WEIGHTS.

Law of Avogadro. From a consideration of the relations existing between the specific gravities and the determined atomic weights of certain elements, Avogadro, an Italian, in 1811 was led to propose the hypothesis *that equal volumes of all gases under like conditions of temperature and pressure contain the same number of molecules.*

The hypothesis uses the word *molecule* in the sense already given and involves the idea that the elements in their internal structures are analogous to compounds and that the molecules of elementary bodies may contain more than one atom, and it will later appear that there are good reasons for such belief. This hypothesis has become of fundamental importance in chemistry in determining molecular weights and settling atomic weights; it is supported by the results of all investigations made to determine the internal structure of gases, and upon the theory of molecular mechanics it affords a mathematical explanation of the laws of compression and temperature, and if the mechanical theory of gases be accepted the hypothesis of Avogadro follows as a mathematical necessity; from these considerations the *hypothesis* is to-day justly considered a *law*.

Accepting the hypothesis as a physical law an important corollary follows directly—viz.: *The molecular weights of substances are directly proportional to their specific gravities in the gaseous state, or the actual weights of the molecules of substances are to each other as the actual weights of equal volumes of the substances in the gaseous state, under like conditions of temperature and pressure.*

Determination of Molecular Weights. It is therefore plain that the weights of the molecules of different gases may be readily obtained in terms of the weight of the molecule of any gas assumed as a standard by simply determining their specific gravities, with reference to the standard gas. It

simplifies the comprehension of the subject here considered to adopt hydrogen as the standard for specific gravities.

To illustrate the above method, let us suppose that a volume of oxygen weighs sixteen times as much as an equal volume of hydrogen, then since these volumes contain the same number of molecules the molecule of oxygen will weigh sixteen times as much as the molecule of hydrogen; or if a given volume of hydrochloric acid weigh 18.25 times as much as an equal volume of hydrogen the molecule of HCl will weigh 18.25 times as much as the molecule of H.

Now if we also take the weight of the hydrogen *molecule* as the standard for molecular weights the molecular weights and specific gravities will be represented by the same numbers, thus, the specific gravity of oxygen referred to hydrogen is 16, the molecule of oxygen weighs 16 times as much as the molecule of hydrogen and if the weight of the hydrogen molecule be taken as unity the weight of the oxygen molecule is 16; therefore when hydrogen is used as the standard for specific gravities and the weight of the hydrogen molecule as the standard for molecular weights the molecular weights and specific gravities are indicated by the same numbers.

Now if we should use *half* the weight of the hydrogen molecule as the standard for molecular weights it is evident that the molecular weights would all be double what they were when we used the whole molecule as the standard and then instead of being indicated by the same numbers as specific gravities the molecular weights would be the doubles of the specific gravities. For reasons which will appear subsequently it is found convenient to use the weight of half of the hydrogen molecule as the standard for molecular weights.

For convenience, we shall, following Prof. Cooke, call the weight of the half hydrogen molecule a *microcrith* and in writing it shall abbreviate it to m. c. Now bearing in mind

that the molecular weights of substances are the actual weights of their molecules in terms of some standard, we may say that the molecular weights of all gases may be obtained in m. c. by doubling their specific gravities referred to hydrogen as the standard; *e. g.*, the specific gravity of HCl is 18.25 the weight of its molecule in m. c. is therefore 36.5—the specific gravity of NH_3 is 8.5 and the weight of its molecule is 17 m. c.

In most cases by chemical analysis we can determine accurately the proportions of the constituents which obtain in any compound, thus, in the case of water, analysis shows that it is composed of one part by weight of hydrogen to eight of oxygen, but this proportion of 1 to 8 holds also with the numbers 2 and 16, 3 and 24, 4 and 32, &c., and from the proportion alone we cannot tell which of the numbers (9, 18, 27, 36, &c.,) is the molecular weight of water vapor, but by finding the specific gravity of water vapor (which is 9) and doubling it, we are enabled to decide that 18 is the molecular weight—that is, a molecule of water vapor weighs 18 m. c.

It should be observed that the determination of the specific gravity of a compound gas is a less accurate operation than the analysis of the gas. The analysis gives an accurate number (the combining number of the gas or gases under consideration) and the specific gravity merely tells what multiple of that number to take.

Thus from the law of Avogadro we are enabled very simply to decide whether a number is the molecular weight or a multiple or sub-multiple of it. This method of determining molecular weights is clearly only applicable to volatile substances, the molecular weights of the non-volatile substances must be determined in other ways.

OTHER METHODS OF DETERMINING MOLECULAR WEIGHTS.

The determination of the molecular weights of substances from their gaseous specific gravities is the most important but not the only method of determining molecular weights. Several other methods have become available but they can only be here mentioned.

Molecular Weights from Osmotic Pressure. The mixing of dissimilar substances, gases, liquids or solids in solution, through membranous diaphragms is in general termed *osmose*. Membranous bodies, such as rubber, parchment, &c., permit the passage of molecules of different substances with very unequal facility. If a solution of a substance be separated from a quantity of the pure solvent by a proper diaphragm or *osmotic membrane*, a certain pressure will be exerted on the membrane from the side of the dissolved substance. This pressure is called *osmotic pressure*.

It has been found that the osmotic pressure is directly proportional to the weight of the dissolved substance in a unit of volume of the solvent and this pressure varies directly as the absolute temperature of the solution. From these and other considerations it seems highly probable that *equal volumes of different solutions at the same temperature and osmotic pressure contain the same number of molecules of the dissolved substances*. From this conclusion it is possible to determine molecular weights. A solution of a solid whose molecular weight is unknown may be prepared so that its osmotic pressure is the same as that of a solution containing a known weight of a solid whose molecular weight is known, the temperatures of the solutions being the same. Then the molecular weights of the solids will be to each other as the weights of equal volumes of the solutions.

Molecular Weights by Depression of Freezing Point. It has been shown that when weights of substances proportional to molecular weights are dissolved in equal weights of the same solvent, they lower the freezing point of the solvent to the same extent. From this generalization it is evident that the molecular weights may be determined. This method is called the *cryoscopic method* of determining molecular weights.

Molecular Weights by Lowering Vapor Pressure. A precisely similar law holds with regard to the effects of a dissolved substance upon the vapor pressure of the solvent. When weights of substances proportional to molecular weights are dissolved in equal weights of the solvent they lower to the same extent the vapor pressure of the solvent. This fact may also be used to determine molecular weights.

Determination of Atomic Weights from Avogadro's Law. From what has been said it is evident that the determinations of atomic weights by the methods thus far given were unsatisfactory because of our inability to decide as to the number of atoms entering the molecule. It will now be shown how we may obtain other information on this point.

Let us compare the gaseous compounds of the elements we are studying with each other. It is evident that a compound molecule must contain at least one atom of each constituent element, therefore, if we find the smallest weight of an element in *any compound* we shall have found its atomic weight.

Take for example the compounds of hydrogen in Table I—in the first column are given the specific gravities, the doubles of these numbers in the second column give the molecular weights in microcriths, in the third column is given the per cent of hydrogen in the molecule, or the proportion which the weight of hydrogen in the molecule bears to the whole weight of the molecule, in the fifth column this weight of hydrogen is given in m. c's.

TABLE I.

	Specific gravities.	Molecular weight in m. c.	Proportion of hydrogen.	Weight of H. in m. c.	Symbols.
Hydrochloric acid,	18.25	36.5	.0274 = $\frac{1}{36.5}$	1	HCl
Hydrobromic acid,	40.5	81.0	.0123 = $\frac{1}{81}$	1	HBr
Water vapor,	9.0	18.0	.1111 = $\frac{2}{18}$	2	OH ₂
Sulphydric acid,	17.0	34.0	.0588 = $\frac{2}{34}$	2	SH ₂
Ammonia,	8.5	17.0	.1765 = $\frac{3}{17}$	3	NH ₃
Phosphorus tri-hydride,	17.0	34.0	.0882 = $\frac{3}{34}$	3	PH ₃
Marsh gas,	8.0	16.0	.250 = $\frac{4}{16}$	4	CH ₄
Olefiant gas,	14.0	28.0	.161 = $\frac{4}{28}$	4	C ₂ H ₄

It is thus seen that the smallest weight of hydrogen in any of these compounds is one m. c., and this is the *smallest weight* yet found in any compound. It also appears from the table that the amounts found in the other compounds are multiples of this small weight.

TABLE II.

	Specific gravities.	Molecular weight in m. c.	Proportion of O.	Weight of O in m. c.	Symbols.
Water vapor,	9	18.0	.8889 = $\frac{16}{18}$	16	OH ₂
Carbon monoxide,	14	28	.5714 = $\frac{16}{28}$	16	CO
Carbon dioxide,	22	44	.7272 = $\frac{32}{44}$	32	CO ₂
Sulphur dioxide,	32	64	.50 = $\frac{32}{64}$	32	SO ₂
Sulphur trioxide,	40	80	.60 = $\frac{48}{80}$	48	SO ₃
Oxygen,	16	32	1.00 = $\frac{32}{32}$	32	O ₂

TABLE III.

	Specific gravi- ties.	Molecular weight in m. c.	Proportion of Cl.	Weight of Cl. in m. c.	Symbols.
Hydrochloric acid,	18.25	36.5	.9726 = $\frac{35.5}{36.5}$	35.5	HCl
Acetyl chloride,	39.2	78.5	.452 = $\frac{35.5}{78.5}$	35.5	C ₂ H ₃ OCl
Carbonyl chloride,	49.5	99.0	.717 = $\frac{71}{99}$	71	COCl ₂
Phosphorus tri-chloride,	68.7	137.5	.774 = $\frac{106.5}{137.5}$	106.5	PCl ₃
Carbon tetrachloride,	77	154	.922 = $\frac{142}{154}$	142	CCl ₄
Chlorine,	35.5	71	1.000 = $\frac{71}{71}$	71	Cl ₂

A similar comparison of the compounds of oxygen and chlorine in Tables II and III, shows that the smallest amounts of these elements which enter are respectively 16 and 35.5 microcriths, and no smaller weights have ever been found to enter; again, all larger amounts are multiples of these smaller weights.

These facts lead irresistibly to the conclusion that these smallest weights are our chemical units or atoms, and the larger amounts are exact multiples because they contain two or more atoms. The law of Avogadro then gives us the means of deciding as to the molecular weights of gaseous substances and by a comparison of the various compounds *we select the smallest weight of an element which enters any compound as the atomic weight.* The number of times this weight is contained in the other molecules gives the number of atoms of the element which enter them.

It can now be seen that had we not taken the weight of the half hydrogen molecule as the standard for molecular weights it would have been necessary to express the smallest amounts of hydrogen which enter certain compounds by $\frac{1}{2}$. Our standard m. c. is the smallest mass of matter which has yet been separated from any compound. It is the chemical atom, and since it is the half molecule, the molecule of hydrogen evidently contains two atoms.

It should be remembered that the atomic weights depend upon the assumption that the same proportions which exist between the constituents of any compound, exist between the

constituents of the molecules of said compound. Such is the only rational assumption, and these atomic weights are the relative weights of the atoms or chemical units of different substances, or the actual weights of the different atoms in terms of the weight of the hydrogen atom taken as unity.

Compounds sometimes contain the elements in other proportions than that of atomic weights, but the variation from atomic proportions arises from the fact that molecules, as already stated, are formed by the union of an atom of one kind with one, two or three of another kind, or two of a kind with three of another, etc., etc. These different proportions are all *combining* or *equivalent* weights, and it is clear that they must be multiples or sub-multiples of the atomic weights. When elements unite in the proportion of one atom to one of another kind, the equivalent weights are the same as atomic weights, but they are different when the atoms unite in other proportions.

The relations between specific gravities and adopted molecular weights are not usually so exact as is indicated in Tables I, II and III. The numbers here given (specific gravities) may be considered as corrected by the results of chemical analysis.

From certain of their volatile compounds, by the application of Avogadro's law, the atomic weights of the following thirty-eight elements have been determined:

Aluminum, antimony, arsenic, boron, bromine, bismuth, carbon, cadmium, chlorine, chromium, copper, fluorine, gallium, hydrogen, indium, iodine, iron, lead, mercury, molybdenum, nickel, nitrogen, osmium, oxygen, phosphorus, selenium, silicon, sulphur, tantalum, tellurium, thorium, titanium, tungsten, vanadium, zinc and zirconium.

By this method alone four of the elements named (aluminum, copper, gallium and iron) have atomic weights double those usually assigned them.

Number of Atoms in Elementary Molecules. When the atomic and molecular weights of an element are known it is evident that the quotient of the latter by the former gives the number of atoms in the molecule. The molecular weights of thirteen of the elements have been determined from their specific gravities in the gaseous state and thence the number of atoms in their molecules. The elements referred to are given in the subjoined table together with the relation between their atomic and molecular weights:

ELEMENTS.	Molecular Weight
	Atomic Weight Number of Atoms in Molecule.
Cadmium,	1
Mercury,	1
Zinc,	1
Hydrogen,	2
Chlorine,	2
Nitrogen,	2
Tellurium,	2
Oxygen,	2
*Bromine,	2
*Iodine,	2
*Selenium,	2
*Sulphur,	2
Phosphorus,	4
Arsenic,	4

It is thus seen that cadmium, mercury and zinc are monatomic and phosphorus and arsenic are tetratomic, the others were diatomic under the conditions of the experiments. Those elements marked with an asterisk varied in specific gravity with certain variations of temperature. Thus, sulphur at a lower temperature had six atoms in a molecule and iodine at a higher temperature than that employed in the table had one atom in the molecule.

Most of the elementary bodies thus appear to be diatomic. That this conclusion is involved in the law of Avogadro may also be seen from the following consideration. It is known that one volume of hydrogen combines with one volume of chlorine to form two volumes of HCl—from the law, each of the two volumes of HCl contains as many molecules of HCl as each of the original volumes contained molecules of H

and Cl respectively; now suppose that the volumes of H and Cl each contain n molecules of H and Cl respectively, the two volumes of HCl must each contain n molecules, and as each molecule of HCl must contain at least one atom of H and one of Cl, there must have been at least $2n$ atoms of each of these elements, and consequently two atoms to each of the n molecules. In the same manner by considering the fact that one volume of oxygen combines with two volumes of hydrogen to form two volumes of water vapor, we arrive at the conclusion that the molecule of oxygen contains two atoms and by similar considerations of certain of their compounds the molecules of nitrogen and sulphur may be shown to contain two atoms.

These are unavoidable conclusions from the law of Avogadro, but there is also some independent evidence that certain molecules of elements contain two atoms. Thus it was found that carbon burned in the protoxide of nitrogen produces more heat than when burned in oxygen. A natural explanation of this fact is found in the supposition that it requires more heat to decompose the molecule of oxygen (it being composed of two atoms) than it does to decompose the molecule of the protoxide of nitrogen. Again, the nascent state which has been referred to as favorable to chemical action may be conceived to be due to the uncombined condition of the elementary atoms when just liberated from some previous combination. Thus, when hydrogen gas is passed through nitric acid it produces no chemical change. The molecules above referred to each have two atoms, but such is not the case with all elementary molecules.

Again, the relations between the specific heats of gases at a constant volume and a constant pressure are not exactly what they should be from a consideration of the external work done; it requires more heat to raise the temperature of a gas under constant volume than it should, in proportion to that required under constant pressure. Now it may be supposed that a portion of the heat is consumed in the first case in producing a motion among the particles of the molecules which does not appear as change of temperature, and if the supposition be correct then the discrepancy referred to should not be observed in a gas whose molecule contains one atom. The relation between the specific heat of mercury vapor at a constant pressure and constant volume was found to accord exactly with theory, which seems to be a physical proof that the mercury molecule has but one atom.

Isomorphous Relations. Bodies which crystallize in the same or in very similar forms are said to be isomorphous, and the fact that many compounds of similar chemical constitution do crystallize in the same form led some chemists to believe that the same crystalline form assured the same atomic constitution of the respective molecules of the substances, that an equal number of atoms arranged in the same way or united in the same way, gave the same crystalline form.

It is now known that when the term *isomorphism* is used in the above sense the conclusion is not warranted. If in addition to the same crystalline form we impose the condition that the bodies under consideration must be capable of replacing each other in the same crystal without destroying the form, the idea of isomorphism becomes much more restricted and the conclusions which result from its application in fixing atomic weights are generally satisfactory. Thus, it is known that aluminum and oxygen unite in only one proportion, 18.3 of aluminum to 16 of oxygen, but this same proportion exists in the numbers of

ALUMINUM and OXYGEN.

36.6	32
54.9	48
73.2	64

and the atomic weight assigned to Al will depend upon the constitution assigned to the oxide—if the oxide be a

			OXYGEN.	ALUMINUM.
<i>monoxide</i> we shall have	Al O	=	16	18.3
<i>dioxide</i> we shall have	Al O ₂	=	32	36.6
<i>trioxide</i> we shall have	Al O ₃	=	48	54.9
<i>sesquioxide</i> we shall have	Al ₂ O ₃	=	48	{ 27.4 27.4

The numbers in the last column are the weights which must be assigned to the atom of aluminum according to the several modes of constitution indicated in the first column.

The constitution of the oxide alone does not enable us to decide between the different formulæ, but as the aluminum oxide is isomorphous with the sesquioxide of iron it is assumed to be a sesquioxide and its atomic weight thus becomes fixed as 27.4.

The utility of this law is limited in application to groups of closely allied substances and its indications become more valuable when connected with conclusions from other physical laws. The law of isomorphism was first enunciated by Mitscherlich in 1819.

Volume Relations of Elements and Compounds. Under the law of Avogadro we have seen that when hydrogen is used as the standard for specific gravities and the half hydrogen molecule as the standard for molecular weights, the specific gravities of gases are the halves of their molecular weights. As most elementary gases are diatomic it follows that the atomic weights and specific gravities of elementary gases are given by the same numbers—one-half their molecular weights. Since specific gravities are given by the weights of equal volumes it follows that equal volumes of elementary gases contain atomic proportions by weight. Atomic proportions being the proportions which combine it likewise follows that *the combining volumes of all diatomic elementary gases are equal*, and if we conceive the smallest combining volumes of such gases to contain only one atom we reach the conclusion that *the ultimate combining volumes of elementary gases occupy equal spaces, or atoms of elementary gases occupy equal spaces*. From the above relations it is readily seen that the number of volumes of the diatomic elementary gases which combine to form a compound gas are indicated by the number of atoms of each element which enter the molecule of the compound gas. Thus, to form

HCl	there are required 1 vol. H and one	vol. Cl
NH ₃	there are required 1 vol. N and three	vols. H
OH ₂ (water vapor)	there are required 1 vol. O and two	vols. H

Research widely extended has proven that with a few exceptions, which may yet disappear, the molecules of compound gaseous bodies occupy twice the space of the hydrogen atom, no matter how many atoms of the elementary gases enter the compound molecule. Thus, each of the molecules HCl , NH_3 , CH_4 , C_2H_4 , CO , &c., occupies twice the space of the hydrogen atom.

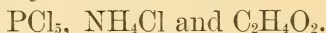
Since the same proportions exist between the quantities of the elements which form the whole body as do between the quantities which form the molecule, it follows that no matter how many volumes of elementary gases combine to form a compound gas of the first order, they are all condensed to two volumes in the compound. All molecules, whether of the first or a higher order, occupy equal spaces, hence the same law of condensation holds in combinations of higher order than the first.

This law of condensation is illustrated in the examples below.

2 vol. H	+ 1 vol. O	give 2 vol. water vapor	= OH_2
2 vol. Cl	+ 1 vol. O	give 2 vol. hypochlorous anhydride	= Cl_2O
2 vol. N	+ 1 vol. O	give 2 vol. nitrogen protoxide	= N_2O
1 vol. Cl	+ 1 vol. H	give 2 vol. hydrochloric acid gas	= HCl
1 vol. N	+ 3 vol. H	give 2 vol. ammonia	= NH_3
2 vol. CO	+ 2 vol. Cl	give 2 vol. carbonyl chloride	= COCl_2
2 vol. C_2H_4	+ 1 vol. O	give 2 vol. ethene oxide	= $\text{C}_2\text{H}_4\text{O}$

Apparent Exceptions to the Law of Volumes.—From the foregoing considerations it is seen that the molecules of gaseous bodies are believed to occupy equal spaces, twice the space occupied by the hydrogen atom, and that their vapor densities referred to hydrogen are the halves of their molecular weights. There are a few apparent exceptions to this law, but the exceptions are believed to be due to molecular changes which take place in the bodies under the influence of heat during the determination of their vapor densities, and that there is no occasion as yet to doubt the validity of

Avogadro's law. Among the bodies which were first thought to be exceptions may be mentioned



The quotient obtained by dividing the atomic weight of a simple body by its density is called the *atomic volume*, and that obtained by dividing the molecular weight of a body by its density is called the *molecular volume*. If matter were continuous these quotients would give the relative volumes of atoms and molecules.

Specific Heats and Atomic Weights. The investigations of Pettit and Dulong in relation to the specific heats of the solid elements developed the fact that *their specific heats are very nearly inversely proportional to their atomic weights*, so that if atomic proportions, by weight, of these different elements be taken the quantity of heat to change the temperature of these proportions through equal intervals is the same in all.

In the following table a number of the solid elements are arranged according to their determined specific heats, beginning with those having the greatest:—

	H	A	H × A
Lithium,	0.941	7	6.6
Sodium,	0.293	23	6.7
Aluminum,	0.214	27.4	5.9
Potassium,	0.166	39	6.5
Iron,	0.114	56	6.4
Nickel,	0.109	59	6.4
Copper,	0.0952	63.4	6.0
Zinc,	0.0955	65.2	6.2
Silver,	0.0570	108	6.2
Tin,	0.0562	118	6.6
Gold,	0.0324	197	6.4
Platinum,	0.0324	197.4	6.4
Lead,	0.0307	207	6.4

In the 1st column are the specific heats, in the 2nd the atomic weights and in the third the product of these numbers; water is taken as the standard of specific heats. This table exhibits the inverse relation existing between atomic

weights and specific heats and the products all fall between the numbers 5.4 and 6.9—the mean value when all the solid elements are considered is usually given as 6.4. It is true that there are variations from this number but the variations are slight and are probably due to the causes which influence the thermal condition of bodies and render the exact determination of specific heats uncertain.

Since the announcement of Pettit and Dulong in 1819, that the atoms of all elements have the same capacity for heat, or the same specific heat, many facts have been accumulated in favor of the generalization and render it very probable that it is correct.

This number (6.4) is frequently called the *atomic heat* of elements.

This law gives us a ready means for the determination of the atomic weights of elements when their specific heats are known, it being only necessary to divide the number 6.4 by the specific heat. However, the difficulty of determining specific heats accurately, limits very much this method of arriving at atomic weights, but the law enables us to decide with certainty between two or more possible hypotheses.

We have seen that analysis will give the proportions of the constituents of a compound with a great degree of accuracy and if we can decide as to the number of atoms of the respective elements in the compound the atomic weights become known, *e. g.*: analysis shows that silver chloride contains 108 parts of silver and 35.5 parts of chlorine—with only this fact we can not tell whether there be one or more atoms of silver, but by dividing 6.4 by the specific heat of silver (.057) we get 112 a number so nearly coinciding with the result of analysis as to show beyond doubt that there is but one atom. As the result of analysis is more reliable than the determination of specific heat we accept 108 as the weight of the atom of silver—the specific heat merely deciding us as to the number of atoms in the compound.

The specific heats of the elementary bodies have not been determined at any common temperature, so that the values found are not strictly comparable. The specific heats of the elements generally vary with the temperature, but there are certain temperature-intervals, different for the different elements, between the limits of which the specific heats are nearly constant. For this interval only is the law of Dulong and Pettit true.

The following forty-nine solid elements have had their specific heats determined directly:

Aluminum	Cobalt	Magnesium	Selenium
Antimony	Copper	Manganese	Silicon
Arsenic	Didymium	Mercury	Silver
Boron	Gallium	Molybdenum	Sulphur
Beryllium	Gold	Nickel	Sodium
Bismuth	Indium	Osmium	Tellurium
Bromine	Iodine	Palladium	Thallium
Carbon	Iridium	Phosphorus	Thorium
Cadmium	Iron	Platinum	Tin
Calcium	Lanthanum	Potassium	Tungsten
Cerium	Lead	Rubidium	Uranium
Chromium	Lithium	Ruthenium	Zinc
			Zirconium

With but few exceptions the product of the specific heat into the atomic weight is approximately equal to 6.4, all falling between 6 and 7. The exceptions are boron, beryllium, carbon, gallium and silicon.

The application of the law of equal atomic heats has been found in many instances to extend to chemical compounds in the case of bodies of similar atomic composition. In such cases the products of the specific heats into molecular weights are nearly constant and are equal to as many times 6.4 as there are atoms in the molecule. If the law were of general application to compounds it would give us obvious means for the determination of the number of atoms in a molecule and a method of general application in determining atomic weights. But the law is not of general application to compounds and can only be used to a limited extent in determining atomic weights.

In the case of the solid elements when their specific heats are determined under specified conditions it may be considered that there are no exceptions to the law of Pettit and Dulong, so closely do the products of the atomic weights and specific heats approximate to a common number. The difficulty of determining how much of the heat transferred to gases and compounds is consumed in performing internal and external work and how much in simply affecting temperature, renders it as yet impossible to bring them under the general law. It is a reasonable expectation that this will be done as our knowledge of molecular structure increases.

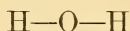
VALENCY OR QUANTIVALENCE.

We have already seen that the atomic and equivalent weights of some of the elements are the same, and in others that the atomic weight is some multiple of the equivalent weight. In other words that atoms of certain elements can only replace or combine with atoms of other elements in the proportion of one to one, in other cases this equivalency or substitution can occur in the proportion of one atom to two or more of another kind—thus, chlorine, bromine and iodine always combine with hydrogen in the proportion of one atom to one, oxygen and sulphur one atom to two of hydrogen, and when sodium acts on hydrochloric acid each atom of sodium replaces one of hydrogen, as $\text{Na} + \text{HCl} = \text{NaCl} + \text{H}$, with zinc under the same circumstances each atom replaces two of H, as $\text{Zn} + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2$. This difference of combining or replacing power has been called *valency*, *quantivalence* and *atomicity*. The first term is deemed best and will be adhered to—the second may be used with propriety—but the third should not be used in this sense.

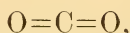
If we select the hydrogen atom as the standard of reference the valency of any other element is known by the number of hydrogen atoms that its atom is equivalent to in the sense just given. The elements have been classed according to degree of valency as univalent, bivalent, trivalent, &c., and are also called monads, dyads, triads, tetrads, pentads, &c.. The elements of even valency are also called *artiads* and those of uneven valency *perissads*. The valency

is sometimes indicated by putting dashes or Roman numerals after the symbols of the elements, thus—O^{II}, C^{IV}, P^V, &c.

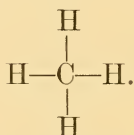
Another method of indicating the valencies of elements and the manner in which they are supposed to be satisfied in combination is by graphic formulæ thus, water may be represented by



and carbon dioxide by



marsh gas by

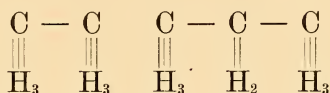


These are called graphic or structural formulæ and indicate nothing more than the degree of valency of the elements and the manner in which they may be supposed to be satisfied in combination.

The valency of an atom as shown by its replacing power corresponds exactly with that shown by its combining power—that is, an atom capable of replacing a certain number of monad atoms is also capable of combining with the same number—thus the atom of zinc which is capable of replacing two atoms of hydrogen is also capable of combining with two atoms of Cl, or Br—monad elements. This property of valence is inherent to radicals, already defined, as well as to elements, and is manifested when they change places in reactions with other radicals or elementary atoms; some radicals are capable of combining with or replacing one monad atom and others more than one.

In the above graphic formulæ it is seen that the units of valency of each atom are represented as satisfied by combination with units of valency of other atoms; such compounds are called normal or saturated compounds and in the molecule of such a saturated compound the sum of the perissad atoms is always an even number. This is the *Law*

of even numbers and it is of necessity true in saturated compounds, from the above definition of such compounds. To form a saturated molecule it is not however necessary that the units of valency of each atom shall combine with the units belonging to atoms of different elements, they sometimes combine with those of other atoms of the same element, thus—



which are saturated hydro-carbons.*

By considering the above formulæ it is evident that if an atom of any kind could be removed the balance of valency would be destroyed and a certain number of units of valency would be left unsatisfied—thus if from the saturated molecule CH_4 we remove one atom of H, we get the compound CH_3 , from SO_3 remove one atom of O and we get SO_2 . These unsaturated molecules constitute the compound radicals already referred to and the valency of a compound radical may generally be said to equal the valency of the atom or atoms which the saturated molecule may be considered to have lost. As already stated, it is only a few of these non-saturated molecules that exist in a free state, as CO, SO_2 , &c., in other cases two of the unsaturated molecules combine with each other, and then again they appear as transferable compounds in chemical reactions without isolation. The tendency of unsaturated radical molecules to combine with each other seems to be analogous to the action of the atoms of elementary bodies—since we have seen that these elementary atoms seldom exist in the free state but are combined in pairs. It may also be stated that generally the combined radicals which exist separately have an even valency.

*It is evident from this consideration that there is a lack of precision in the definition of a “saturated molecule.” Other definitions have been proposed but are upon the whole not more satisfactory.

Variable Valency. The valency of an element is not a fixed and unvarying property. Many of the elements exhibit varying degrees of valency as is especially shown by their varying degrees of combining power—thus tin forms two compounds with Cl—viz.: SnCl_2 and SnCl_4 and phosphorus forms PCl_3 and PCl_5 , numerous other examples might be given. Compounds formed under these varying influences are often as different from each other as are the compounds of different elements and hence arises the difficulty of classifying the elements according to their valency. However, of the different degrees of valency shown by the same element some one degree is generally more common and the compounds resulting from its action more permanent than any other and in several elements, as H and the alkaline metals, the valency has been found invariable.

Of the multivalent elements the variation in valency usually takes place by a loss or gain of two units of valency, so that the possible conditions of the same element are usually all even or all odd, thus, *Cl* may be univalent, trivalent, quinquivalent and septivalent. *S* may be bivalent, quadrivalent or sexvalent.

It is at present impossible to account for these variations but as a general rule the compound in which the valency of a polygenic element is most completely satisfied is the most stable and the others tend to pass into this one. From these considerations it is evident that the valencies of most of the elements are not fixed and the conditions of the variations are not known. From a consideration of all the facts the most logical conclusion is that the valency is, like affinity, a relative property of the atoms, depending upon a variety of causes, among which may be classed the mutual influence of the atoms on each other, the relative quantities of the acting substances and the temperature. It may also be observed that the theory of valency reiterates the law of multiples, which is the simple statement of an experimental fact.

Valency and Affinity. Valency and affinity are properties inherent in the atoms and as yet understood, are distinct and different properties. Affinity has reference to the force with which atoms or molecules attract each other and is approxi-

mately estimated by the thermal effects of their combinations. Valency has reference only to the saturating capacity in combination or replacement and irresistibly introduces the idea of arrangement of atoms in the molecule.

The abstract idea of valency has reference only to the numerical capacity of saturation, but the concrete conception sees each body characterized by a particular order in combination and every molecule of a definite structure. The theory of valence then finds application in expressing the relations between the atoms of molecules and in allowing conception of the relative constitution of bodies. Again, from knowledge of the more common valency of elements the theory is of great importance in expressing all ordinary reactions, the results of the general laws of combination.

RELATIONS BETWEEN THE ATOMIC WEIGHTS AND PROPERTIES OF THE ELEMENTS.

Although atoms are hypothetical masses and are beyond direct observation, their relative weights, as has been stated, are the constants of chemistry and are indispensable to analysis and stoichiometrical research. It now seems possible that these numbers may become equally important in all branches of physical science, for recent investigations point to an interdependence, more or less complete between the atomic weights and physical properties of the elements. In 1815, Prout brought forward the view that the matter of which all elements are composed is hydrogen and that the atomic weights of all other elements are entire multiples of the atomic weight of hydrogen and this has been known as Prout's Law.

The investigations of Stas of Brussels, undertaken for the purpose of testing Prout's Law are frequently held to invalidate it, but so large a majority of the atomic weights are so nearly exact multiples of that of hydrogen, that it can hardly be the result of chance, and Prout's view is still believed by many chemists to have a high degree of probability. It has also been long known that the atomic weights of many allied elements have certain simple numerical relations, but Newlands was the first to point out the fact that the elements, when arranged in numerical order of their atomic weights, exhibit a periodic recurrence of similar properties. This Law of Periodicity may be illustrated by a consideration of the first fourteen elements after hydrogen, and is most evident if we consider the atomic volumes of the solid elements in connection with their atomic weights.

The atomic volume, as already stated, is obtained by dividing the atomic weight by the density of the element. The elements referred to are here arranged in order of their atomic weights and immediately beneath each is written its atomic volume, then its density,

Li = 7	Gl = 9.0	Bo=11	C=12	N=14	O=16	Fl=19
V =11.9	5.6	4.0	3.6	?	?	?
D = 0.59	1.64	2.68	3.3			
Na=23	Mg=24	Al =27.3	Si=28	P=31	S =32	Cl=35.5
V =24	14	10	11	16	16	27
D =97	1.75	2.67	2.49	1.84	2.06	1.38

The atomic volumes of the elements thus gradually decrease toward the middle of the series and then increase. The densities of the elements increase toward the middle and then decrease. The volatilities of the elements also diminish toward the middle and then increase. The more common valencies of the elements increase toward the middle of the series and then decrease. In addition to these properties others, as the malleability, fusibility, conductivity, refractive power and heat of combustion, also appear to be closely connected with their atomic weights. Mendelejeff and others have shown that the entire list of elements can be thus arranged in series and that the properties of the elements are in periodic relations with their atomic weights. The classification of the elements cannot be properly discussed without a fair knowledge of the subject matter of chemistry, and this discussion is accordingly not essential to that knowledge, but the probabilities in favor of the Periodic Law are great, and it promises, at no distant day, to furnish a new basis for physical investigation as well as for a classification of the elements.

STOCHIOMETRY.

That class of chemical computations which can be made from a consideration of the numerical relations of atomic weights and the volume relations of elements and compounds is called *stochiometrical*. From a knowledge of preceding principles many such computations are possible. It has already been stated that the symbols of the respective elements represent atoms and that the atoms of different elements have different weights—that the molecular weights of substances are the sums of the weights of the atoms in their respective molecules. In the most limited sense chemical symbols represent atomic weights of their respective elements in terms of the weight of the H atom, but in a more general sense, in all equations, reactions and formulæ they stand for quantities *proportional* to atomic weights and when the amount by weight of any one element in a formula or

equation is given the amounts of all the others become known.

Percentage Composition. Thus, the formula for water is OH_2 and from the relations expressed in the formula if either the amount of H or O is assumed the amount of the other element is also known.

From the formula of a substance it is evident that we may also readily compute its percentage composition—thus, the formula of alcohol is $\text{C}_2\text{H}_6\text{O}$ —the molecular weight is 46, hence in 46 parts by weight of alcohol there are—24 of C

$$\begin{array}{r} 6 \text{ of H} \\ 16 \text{ of O} \\ \hline 46 \end{array}$$

hence in 100 parts we should have

$$\begin{array}{l} \text{for C } 46 : 24 :: 100 : x = 52.18 \\ \text{for H } 46 : 6 :: 100 : y = 13.04 \\ \text{for O } 46 : 16 :: 100 : z = 34.78 \\ \hline 100.00 \end{array}$$

Having given the percentage composition of a substance we can also readily determine the numerical relations existing among the atoms but not necessarily the actual number of atoms in the molecule—thus the percentage composition of acetic acid is

$$\begin{array}{l} \text{C} = 40 \\ \text{H} = 6.67 \\ \text{O} = 53.33 \\ \hline 100.00 \end{array}$$

since these numbers are the relative weights of the elements in the substance if we divide them by the atomic weights the quotients will express the relations existing among the numbers of atoms of the different elements. Performing the division referred to we have for the numerical relation of atoms



which is evidently the same as



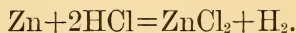
Empirical and Molecular Formulae. The simplest expression for the numerical relations existing among atoms of a molecule of a substance is called its *empirical* formula; that is to say, when we express the numerical relation among the atoms by the smallest numbers possible; thus above $\text{C}_1\text{H}_2\text{O}_1$ is the empirical formula for acetic acid. The same relations exist among the numbers of atoms whether the formula be $\text{C}_1\text{H}_2\text{O}_1$, $\text{C}_2\text{H}_4\text{O}_2$, or $\text{C}_3\text{H}_6\text{O}_3$, &c.

The formula which gives the exact number of atoms of each of the elements which enters the molecule of a substance is called the *molecular* formula. It can not be computed with certainty from the percentage composition alone, but if the molecular weight of the substance is known the problem admits of definite solution, for from the molecular weight we know the sum of the atomic weights and can decide which of the formulæ expressing the numerical relations among the atoms is the molecular formula.

Thus, in the example above the molecular weight of the acetic acid is 60, hence it is evident that of the possible formulæ $\text{C}_2\text{H}_4\text{O}_2$ is the molecular formula of the acid. The molecular formula is always the same as, or a multiple of, the empirical formula.

Problems Involving Weights. Since, as has been said, in the most general sense the symbols represent quantities proportional to atomic weights and formulæ represent quantities proportional to molecular weights it is easy to determine the amounts of the various substances indicated in any equation when the amount of any one is assumed. For this purpose it is only necessary to express the atomic and molecular weights of the different terms of the equation and simple proportions will solve the problem.

Thus, in the equation



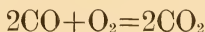
expressing the action of Zn upon HCl, suppose we assume that Zn stands for 10 ounces of zinc—then to determine how much HCl is indicated we proceed as follows: the atomic weight of Zn=65.2 and the molecular weight of HCl=36.5. The reaction indicates that for the transformation of 65.2 parts of Zn there are required $2 \times 36.5 = 73.0$ parts of HCl—hence the amount to transform 10 parts of Zn would be determined by the proportion

$$65.2 : 73 :: 10 : x.$$

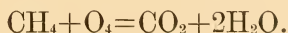
The amounts of the other substances involved in the reaction under the supposition that 10 ounces of zinc are employed would be determined in exactly the same manner.

It matters not whether some of the terms of the equation are simple atoms or whether all the terms are composed of molecules. The molecular and atomic weights of the different terms express the relations existing between the amounts of the substances employed in the reaction and from these relations the amounts of all the substances indicated can be determined when the amount of any one is assumed.

Problems Involving Volumes. All of the above solutions depend upon the numerical relations of atomic weights but a chemical equation expresses not only relative weights but also relative volumes of the reagents and products when in a state of gas. We have seen that all gaseous molecules occupy equal spaces and that gaseous atoms occupy one half the space of the molecule, coupling these facts with the principles of notation explained it is evident that the relative numbers of volumes in an equation of gaseous terms can be read off directly—thus



and



In the first equation, since molecules occupy equal spaces, it is seen that the number of volumes of CO_2 is the same as the number of volumes of CO and the number of volumes of O

involved is one half that of the other gases.—In the second equation the relative volumes are, one of CH_4 , two of O , one of CO_2 and two of OH_2 (vapor of water).

It is often desirable to pass from volumes to weights or the reverse in the case of gaseous bodies. The problem is so simple as to require only the statement that in the first case we multiply the number of volumes by the weight of a unit of volume and in the second case we divide the weight by the weight of a unit of volume; volumes, of course, being always taken under standard conditions of temperature and pressure.

CHEMISTRY OF THE NON-METALS AND THEIR COMPOUNDS.

OXYGEN.

Oxygen is the most abundant and widely distributed of the chemical elements. It exists in the uncombined state in atmospheric air forming about one-fifth of its volume; it is there mixed with nitrogen which constitutes nearly the entire bulk of the remaining four-fifths.

In the free state oxygen is an essential to all forms of life.

In the combined form it is an important constituent of most of the mineral and organic substances. In this form it constitutes eight-ninths, by weight, of water and about one-half, by weight, of silica and of the various silicates and limestones, which compose by far the greater portion of the earth's crust.

Oxygen was discovered by Priestly in England in 1774 and called by him dephlogisticated air. In the following year it was independently discovered by Scheele in Sweden. It was named *oxygen* by Lavoisier.

Physical Properties. Oxygen is a gas tasteless, odorless, colorless, and perfectly transparent. It is slightly soluble, water at 60° F. dissolving about .03 of its volume. By great pressure and low temperature it has been liquefied and by further cooling solidified. Its specific gravity referred to hydrogen is given by its atomic weight; it is thus seen to be slightly heavier than atmospheric air; when liquefied it is lighter than water.

Chemical Properties. Oxygen is remarkable for the wide range of its chemical action. With the exception of bromine it forms compounds with all other elements and with the exception of six elements it unites directly (that is without the intervention of a third substance).

These combinations as already stated are called oxides and the process is termed oxidation.

The combination of oxygen with the other bodies is always accompanied by the development of heat but if the oxidation is very slow the heat may not be perceptible. If the oxidation be sufficiently rapid to produce light and heat it becomes a case of combustion.

Combustion in a general sense is any chemical action accompanied by heat and light; all ordinary cases of combustion in air are processes of oxidation, the light and heat being the result of the chemical union of the oxygen with the body burned. In most cases an elevation of temperature is necessary to bring about the union of oxygen with other substances; with some bodies at ordinary temperature it unites slowly without sensible elevation of temperature, and with a few rapid oxidation takes place producing combustion.

Action on Non-Metals. Among the non-metals phosphorus is the only element that combines with oxygen at the ordinary temperature. In the air it gives off white fumes and emits a pale phosphorescent light. It is then undergoing oxidation and if it be finely divided true combustion will result. This may readily be accomplished by dissolving a little phosphorus in carbon disulphide and pouring the solution on blotting paper; when the solvent evaporates, the finely divided phosphorus exposes a large surface to the action of the air, and the paper being a bad conductor the temperature rapidly rises and brilliant combustion results. In warm air a very slight elevation of temperature will cause phosphorus to burn and this is sometimes brought about by

the oxidation of the outside particles; phosphorus must accordingly be handled with great care.

Phosphorus produces a bright light when burning in the air but the brilliancy is greatly increased when it is burned in pure oxygen due to the more rapid combustion and consequent higher temperature.

All substances which burn in air burn far more readily in pure oxygen. By the combustion of phosphorus in air phosphoric oxide is produced (P_2O_5) which may be seen to rise in clouds from the burning phosphorus. This oxide is readily absorbed by water forming phosphoric acid.

If a piece of wood charcoal be heated to redness at a single point and be plunged into a jar of oxygen brilliant combustion takes place, the oxygen combining with the carbon producing carbon dioxide (CO_2) which is a colorless gas. Pure carbon has to be heated very highly before it will combine with oxygen and then the combustion is unattended with flame.

Sulphur burns in air with a blue light when its temperature is raised to about 500° F. In pure oxygen the brilliancy is much increased; in each case the product of combustion is sulphur dioxide (SO_2) which readily unites with water forming sulphurous acid.

Action on Metals. Several of the alkaline and alkaline earth metals (potassium, sodium, lithium, barium, calcium, and strontium) are readily oxidized in the air.

Other of the common metals as iron, lead, and mercury are scarcely acted upon by dry air, and gold, silver, and platinum not at all. Under the influence of high temperature many of the metals burn readily. A magnesian ribbon will burn in air if the end of the ribbon be heated in a Bunsen burner; the light is almost insupportable to the eye. The burning of iron is also easily accomplished and is best shown in a small way by wrapping one end of a softened steel watch spring spirally around a little cylinder of char-

coal and attaching the other end to a suitable holder, igniting the charcoal and plunging the whole into a jar of oxygen. It burns very brilliantly sending off a shower of sparks. The black oxide of iron Fe_3O_4 is produced by the combustion.

Zinc may be burned by a precisely similar arrangement giving (ZnO) zinc oxide.

Iron can be prepared in such finely divided form that when exposed to air it will take fire spontaneously; it is then called pyrophoric iron.

The preceding illustrations which might be extended indefinitely are all cases of oxidation, and it is seen that oxidation may or may not produce the phenomenon of combustion. All ordinary combustion in air is but the oxidation of the body burned, oxygen being the sustaining principle of such combustion and also of animal life. All bodies which burn in air burn with increased splendor in pure oxygen.

It is well here to recall the important fact already stated that the oxides of the non-metals are generally acid oxides and of the metals basic oxides. The former when acted upon by water give the substances which we have defined as acids and the latter tend to neutralize these acids. So general is this tendency of the metallic oxides that any substance which forms a basic oxide may be defined as a metal, though it is not decided that every metal forms a basic oxide.

Preparation of Oxygen. For laboratory and experimental purposes oxygen is most readily prepared from potassium chlorate (KClO_3) or manganese dioxide (MnO_2). From either of the substances oxygen may be obtained by heating in suitable apparatus the results being indicated by the following reactions; KClO_3 (heated) = $\text{KCl} + \text{O}_3$, 3MnO_2 (heated) = $\text{Mn}_3\text{O}_4 + \text{O}_2$.

To accomplish these results a higher degree of heat is required than is convenient and it is customary and advisable to mix with the chlorate from one-fourth to one-fifth its



FIG. 1

Preparation of Oxygen

F Florence Flask

B Bunsen Burner

T Water Tank

G Bell Glass

weight of the oxide when the liberation of oxygen takes place at a lower temperature than when either substance is used alone. The mixture of potassium chlorate and manganese dioxide may be heated in a glass retort or Florence flask, the retort or flask being closed by a perforated cork into which fits a short glass tube. A rubber tube connects with the glass tube and serves to convey the gas to a gas holder or to a jar filled with water standing on a bee-hive shelf. The manganese dioxide, or pyrolusite as it is called in mineralogy, is not changed in this operation. The action of the manganese dioxide comes under the term of catalytic action and is not thoroughly understood but the oxide probably passes to a higher state of oxidation and is then reduced.

Oxygen may also be prepared by the decomposition of water (H_2O) by electricity. In some laboratories both oxygen and hydrogen thus obtained are kept on hand in large holders, the electricity being supplied by dynamo-machines.

Oxygen may be prepared on a large scale directly from the atmosphere by passing a current of air over a mixture of caustic alkali and manganese dioxide; alkaline manganates are thus formed. By passing steam over the heated manganates they are resolved into the original constituents with the liberation of oxygen. The operation can be made continuous.

There are many other methods by which oxygen may be prepared. Priestly when he discovered oxygen obtained it from the red oxide of mercury.

OZONE.

Ozone was discovered by Schonbein in 1840. It appears to be a modified form of oxygen in which it is believed that there are three atoms in the molecule instead of two as in ordinary oxygen. According to Avogadro's law it should be one and a half times as heavy as common oxygen and this has been determined to be the case by experiment. It exists in very small quantity in the atmosphere and is found in the purer air of the country or the seaside more than in thickly populated places. It has been estimated to constitute not more than one volume in a million volumes of air.

Physical Properties of Ozone. Under ordinary conditions ozone is a transparent gas showing a blue tinge when viewed along a glass tube a meter in length. The color deepens by pressure. The gas has a peculiar and distinct odor. It is more easily liquefied than pure oxygen and the liquid has a blue color. When heated to 300° F. ozone is converted into oxygen with an increase of half a volume.

Chemical Properties. Ozone is chemically much more active than oxygen combining with many substances that oxygen will not affect. It will decompose potassium iodide liberating the iodine. In the presence of alkalies it will unite with nitrogen and convert it into nitric acid. It will oxidize silver and also a solution of indigo, bleaching the latter; ordinary oxygen does not act upon these substances. Ozone acts upon many organic substances and it is to this fact that its beneficial effect in the air is attributed. In most cases of oxidation the remaining oxygen appears to be the same in volume as the original ozone. Air highly charged with ozone can not be breathed with impunity, its action on the system resembling that of chlorine.

Preparation of Ozone. Ozone is produced by the passage of electric sparks through the air or oxygen and is generally observed by its odor when a spark electric-machine is operated in the air. It is also produced during the decomposition of water by electricity, by the slow oxidation of phosphorus and turpentine in the air. This latter fact has been suggested as an explanation of the acknowledged salubrity of pine regions.

The presence of ozone may be detected by bringing into it a piece of paper moistened with a solution of starch and potassium iodide; the ozone liberates the iodine which gives a blue color with the starch. The test however does not insure the presence of ozone as certain other substances will have the same action, among these are chlorine, bromine, and nitrogen dioxide.

HYDROGEN.

Hydrogen rarely occurs in a free state under terrestrial conditions, though it has been found to a limited extent in certain volcanic emanations, in the gases given off by oil wells, and occluded in certain meteorites.

The spectroscope has shown it to be present in the atmosphere of several of the heavenly bodies, especially the sun.

Hydrogen was discovered by Cavendish in 1766 and called by him inflammable air; it was subsequently named hydrogen by Lavoisier.

Physical Properties. Hydrogen is a transparent gas, tasteless, colorless, and odorless. It is the lightest substance known. Water is 11160 times as heavy as hydrogen at 0° C. It is not poisonous though animals can not live in this gas alone, oxygen being necessary to life. Hydrogen being the lightest substance known it is conveniently taken as the standard for the specific gravity of gases—that is to say the standard to which other gases and vapors are referred.

Owing to its great lightness hydrogen can be collected by downward displacement or poured upward from one vessel to another; on account of this property it is employed for filling balloons.

Hydrogen is slightly soluble, water dissolving .02 of its volume at 0° C. and 30" barometric pressure.

By great pressure and cold, hydrogen has been liquefied, giving a steel blue liquid. The conducting power of hydrogen for heat is, according to Magnus, greater than that of any other gas. Another remarkable physical property is its great power of passing through animal and vegetable membranes and porous substances generally. This property is called diffusive power and it is a physical property common to all gases and vapors. The diffusive powers of gases are found to be inversely proportional to the square roots of the densities of the gases. Hydrogen accordingly diffuses far more rapidly than any other gas; because of this property hydrogen is more difficult to confine than any other gas. It will leak through a stop cock which will retain oxygen and nitrogen and it cannot be kept long in rubber bags, bladders, &c.

The diffusive property of gases causes them to fill uniformly any space in which they may be placed. It also causes gases to mingle uniformly even against the force of gravity; thus if two vessels one containing oxygen the other hydrogen, be connected by a narrow tube with the oxygen below, in a short time they will be uniformly mixed.

The same result follows with any two gases that do not act chemically upon each other.

The remarkable diffusive power of hydrogen may be shown by the following experiment—take an unglazed porous cup (a common battery cup answers well) and close the open end with a cork through which extends a glass tube; then invert this cup and insert the tube into a tightly sealed bottle arranged with a jet tube as shown in figure I. By placing a glass jar containing hydrogen over this cup the liquid may be forced out of the lower vessel in a jet several feet high. In this experiment the oxygen in the lower vessel passes out through the porous pot into the hydrogen jar, but the hydrogen passes in much more rapidly and the pressure of the hydrogen added to that of the oxygen in the bottle drives out the water. The true diffusion of gases depends upon the motion of their molecules, but this diffusion is often complicated by the nature of the septa through which diffusion takes place. If the diaphragm exerts an adhesive or liquefying action on the gases, or if it is moistened with any liquid which exerts a solvent power on them, the simple diffusion passes into osmose or osmotic action.

These processes are very important in nature; by true diffusion the uniform composition of the atmosphere is mainly maintained and the accumulation of noxious gases prevented, by osmose the function of respiration is performed and the aeration of the blood accomplished. Certain of the metals as platinum and palladium possess the power of absorbing and condensing within their pores large volumes of some of the gases. This action is called occlusion of gases. Certain meteorites have been found to contain a large amount of hydrogen indicating that they have come from regions where hydrogen exists at greater pressure than in our atmosphere.

The terms osmose and diffusion are also applied to the processes by which substances dissolved in liquids pass into solutions of less density through diaphragms or against the force of gravity.

Chemical Properties of Hydrogen. The chemical properties of hydrogen cause it to combine readily with several of the non-metals but it shows little if any disposition to combine



FIG. 2.
Diffusion of Gases.

with metals. The most evident chemical characteristic of hydrogen is its disposition to burn in oxygen. These gases may be mixed in any proportion and they will not act on each other at ordinary temperature, but if a jet of hydrogen issuing into oxygen or air be touched with a flame it takes fire and burns producing great heat but very little light, the flame being barely visible. The result of the combination of hydrogen and oxygen is water as may readily be shown by holding a glass tube over the flame when moisture rapidly deposits on the side of the tube.

Since hydrogen is inflammable and burns in the air it might be expected that it would not support the combustion of bodies which burn in oxygen. This may be proven by inserting a lighted taper into an inverted jar filled with hydrogen. The flame of the taper will be extinguished and the hydrogen will take fire and burn at the mouth of the jar.

If a mixture of oxygen and hydrogen in certain proportion be raised to the temperature of ignition, which can be done by an electric spark or a flame, chemical union at once follows attended by violent explosion. This property of the gases makes great care necessary in experimenting with a mixture of them.

Hydrogen weight for weight, produces more heat in burning than any other substance. One pound of the gas in burning to water produces 34,462 units of heat. The explosion of the mixture of hydrogen and oxygen is of course due to the high temperature which results from the great heat of the chemical union, the heat expanding greatly the water vapor formed by the combination. The most violent explosion occurs when the gases are mixed in the proportion of two volumes of hydrogen to one of oxygen a fact shown by the formula of water. If air be used instead of oxygen the explosion will be less violent due to the presence of the inactive nitrogen.

Owing to its tendency to combine with oxygen when

heated, hydrogen will take oxygen from many other bodies containing it. This removal of oxygen is designated as a *reducing* or *deoxidizing* process and the body accomplishing it is called a *reducing* or *deoxidizing* agent. Thus most of the metallic oxides are reduced at a red heat by hydrogen, which is one of the best reducing agents; for example $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$. On the other hand a body which gives oxygen to another body is called an *oxidizing* agent.

Preparation of Hydrogen. The process by which hydrogen is usually prepared for laboratory purposes is to act upon dilute sulphuric acid with zinc. The zinc decomposes the acid with liberation of hydrogen and formation of zinc sulphate as indicated by the following reaction $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$.

For this purpose the zinc is cut into small strips or granulated by pouring melted zinc into water from a moderate height; a greater surface is thus exposed for contact with the acid. If the sulphuric acid is too strong the zinc sulphate formed does not readily dissolve off the zinc and the chemical action is retarded or stopped. On the other hand if the zinc be pure, it will scarcely act upon the acid; the action is generally facilitated by lead or other metal impurities which have an electrical effect not yet described.

This method of preparing hydrogen can be followed in common Woullf bottles, shown at A in the figure. The zinc is put into the bottle and the acid added at B; the hydrogen is passed out at the tube C and collected by displacement as described under oxygen. Hydrochloric acid may be used to replace the sulphuric in this process or iron may be used instead of the zinc, but the hydrogen from iron is generally less pure than that from zinc.

Hydrogen may also be prepared by passing steam over iron turnings contained in a tube heated to redness. The

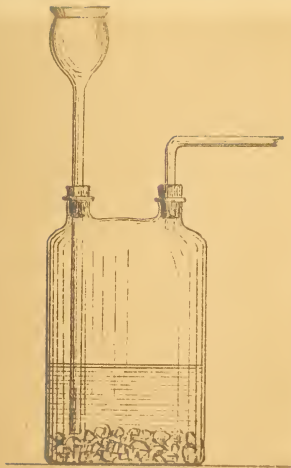


FIG. 3
Woulfe's Bottle.

oxygen of the steam combines with the iron and the hydrogen passes on through the tube— $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$.

It will be observed that the physical properties of hydrogen place it with the non-metals while the chemical properties ally it to the metals.

NITROGEN.

Nitrogen occurs free in the atmosphere of which it constitutes about four-fifths, oxygen constituting nearly the whole of the remaining one-fifth. It also occurs in the volcanic gases, in the atmosphere of the sun, and in certain nebulae, and has been found in meteorites. In the combined form it exists as nitrous and nitric acids, in the compounds of ammonia, and in the organisms of plants and animals.

Nitrogen was discovered by Rutherford of Edinburgh in 1772.

Physical Properties. Nitrogen is a colorless, transparent, odorless, and tasteless gas. Water at 60° F. dissolves less than .015 its volume. By great cold and pressure it has been liquefied and solidified.

Chemical Properties. In its chemical deportment nitrogen is very inert. It combines directly with only a few elements among which may be mentioned silicon, boron, magnesium, carbon, oxygen, and hydrogen; with the last named it combines when one or both elements are in the nascent state to form ammonia (NH_3).

It has no positive poisonous properties but is incapable of supporting respiration or combustion, oxygen being essential to these processes.

Its presence in the atmosphere moderates the action of pure oxygen.

The slight affinity existing between nitrogen and the other elements gives a characteristic property to its compounds many of which are very unstable; thus the nitro-

genized principles of plants and animals are prone to decomposition and many artificial compounds of nitrogen are highly explosive.

Preparation of Nitrogen. Nitrogen is generally obtained in small quantity by burning phosphorus in air confined over water. A porcelain capsule containing phosphorus is floated on the water, the phosphorus is ignited and the whole covered with a bell jar. The burning phosphorus unites with the oxygen forming phosphoric oxide (P_2O_5) which after a time is absorbed by the water.

In larger quantity it may be prepared by passing air over finely divided copper heated to redness in a porcelain tube. The oxygen is removed by the copper.

One of the easiest methods of preparing pure nitrogen is to heat in a glass retort potassium nitrite and ammonium chloride— $KNO_2 + NH_4Cl = KCl + 2H_2O + N_2$.

ATMOSPHERIC AIR.

The gaseous envelope surrounding the earth consists essentially of a mixture of nitrogen, oxygen and argon together with small but variable quantities of carbon dioxide (CO_2), and water vapor with traces of other substances due to accidental or local causes; among the latter may be mentioned ammonia (NH_3), marsh gas (CH_4), sulphuretted hydrogen (SH_2 , and sulphur dioxide (SO_2), the last two may generally be detected near cities and towns. Argon has been only recently discovered and constitutes about one per cent. of the atmosphere. The thickness of the earth's envelope is estimated to be about forty-five miles measured from the earth's surface. The air probably extends beyond this height but is in an extremely rarefied condition.

Physical Properties. The density of the air according to the law of Boyle rapidly diminishes with the height. Due to its weight the atmosphere exerts a pressure on all bodies. The assumed average pressure of the atmosphere at the sea

level has been generally adopted by engineers as the unit of pressure and this unit is named an *atmosphere*. The pressure is generally expressed in terms of the barometric column, that is the height of the mercury column which the air will support.

In British measure an atmosphere is equivalent to the pressure of 29.905 inches of the barometer at 32° F. at London and is very approximately 14.73 pounds on the square inch of surface. In the metric system the *atmosphere* is .00032 greater than in the British.

For all ordinary chemical calculations it may be taken that water is 773 times as heavy as air, both taken at common standard temperature and pressure.

Composition of the Atmosphere. We owe to Cavendish, 1781, the first accurate determination of the proportions of the essential constituents of the atmosphere (N and O). These gases are mixed in the air very approximately in the proportion of 21% of oxygen and 79% of nitrogen by volume and 23% of oxygen and 77% of nitrogen by weight. There is but very little variation in the proportions of these constituents from whatever source the air is obtained.

The proportion of the oxygen and the nitrogen can be very approximately found by passing air over very finely divided copper contained in a glass tube, carefully weighed, and heated to redness; the nitrogen is made to pass into an exhausted globe. The increase in weight of the tube gives the weight of the oxygen and of the globe the nitrogen.

The other two all pervading constituents of the air are water vapor and carbon dioxide; these vary with conditions.

Carbon Dioxide of the Air. The amount of carbon dioxide (CO₂) in the air varies slightly with the locality and with the season, being greater nearer centres of population than in the country and greater in winter than in summer. In the country a greater amount has been found in the air at night

than during the day, the difference being due to the different action of plants during the day and night; this diurnal variation is not observed at sea.

The amount of carbon dioxide in normal air is from three to four volumes in 10000. In cities, in winter and especially, in heavy fogs which prevent diffusion, it may rise to six or seven volumes in 10000. The amount of carbon dioxide though relatively very small is actually very great.

Upon this gas the vegetable kingdom is dependent for its existence; plants by the aid of sunlight decompose the carbon dioxide retaining the carbon and returning the oxygen to the air. On the other hand all animal respiration and all ordinary combustion take oxygen from the air and return to it carbon dioxide. Owing to this cyclic process the change in the proportion of these constituents in the atmosphere must be very slow.

The quantity of aqueous vapor in the air is far less constant than the carbon dioxide. This quantity varies primarily with the temperature of the air as already explained in the subject of heat. The other important circumstances which affect the quantity are the prevailing direction of the winds, the configuration of the land, and the nearness of the bodies of water. Upon the average the aqueous vapor is from 1 to 1.5 volumes to 100 of air.

Other Gaseous Constituents of the Air. Ozone can nearly always be detected in normal air and its presence is more common in the purer air. Hydrogen dioxide is also very generally present in the air and its chemical actions are in many cases analogous to those of ozone and it is difficult to distinguish between the two. Ammonia or more generally its carbonate is nearly always present in minute but variable quantity in the air. The ammonia results from the decomposition of the organic matter and in the presence of moisture combines with the carbon dioxide and other acids present in the air; the nitrates and nitrites of ammonium are sometimes from this source present in the atmosphere.

Other gases occur locally in minute quantities in the air, the most common of which have already been mentioned as sulphuretted hydrogen, sulphur dioxide, and marsh gas.

Solid Constituents of the Air. In addition to its gaseous constituents, minute particles of solid matter are suspended in the air and generally termed dust. Atmospheric dust is made up both of inorganic and organic matter. The inorganic matter is composed of various mineral compounds. The organisms are the propagators of mould, mildew, fermentation and putrefaction, and it is probable that the last named are the agencies through which certain diseases are spread.

COMPOUNDS OF HYDROGEN AND OXYGEN.

WATER.

Water is the most important compound of hydrogen and oxygen. With the exception of the air no substance is so indispensably necessary to terrestrial life as water. Its distribution is only second to that of the air and its absolute amount is enormously greater. Water is the cause of many of the most striking physical phenomena in nature and its uses for economical and domestic purposes are innumerable. Besides the enormous quantities which are spread over the surface of the earth and distributed as vapor through the air, it is an important constituent of all living beings and of many minerals.

The composition of water was first discovered by Cavendish in 1781.

Physical Properties of Water. Many of the physical properties of water are well known, a few will be mentioned here. Thick layers of water have a blue color. Water has greatest density at 4° C. or 39.4° F. In freezing water expands by .09 of its volume so that eleven volumes of water become twelve volumes of ice. The melting point of ice under constant pressure is constant (0° C.=32° F.) but water may be cooled below this point and still remain liquid.

Water evaporates at all temperatures, and ice at temperatures below 0° C. will give off vapor without melting.

The absolute boiling point of water or the temperature above which it can not exist as a liquid is about 1076° F. (580° C). As already stated water at maximum density is taken as the standard for the specific gravities of bodies in general and it is also the standard for the specific heats of bodies in general. One volume of water at the boiling point and under the standard pressure yields 1696 volumes of vapor at the same temperature and pressure, the specific gravity of the vapor being 0.622 (air=1).

Solvent Power of Water. This power of water is not thoroughly understood. It may be defined as the power of water to form a homogeneous liquid with another substance brought into it. Thus many substances, gases, liquids, or solids brought into water disappear and a homogeneous liquid results. The results of these actions are such that the constituents can not be separated by purely mechanical means. The substance thus mingled with the liquid is said to be dissolved by it or in solution in the water. As already stated these solutions differ from mere mechanical mixtures and also to a certain extent from true chemical compounds.

If a very small amount of the substance be dissolved in the water the solution is said to be dilute; when a large amount is dissolved it is a concentrated solution; and when the water will dissolve no more of the substance it is a saturated solution. There is no limit to the extent to which every solution may be diluted but in the case of gases and solids and of most liquids there is a limit to the amount of the substance that may be brought into solution; but some liquids dissolve each other in all proportions, for example water and alcohol.

Solution of Solids. The quantity of a solid required to produce saturation generally varies with the temperature, most solids being more soluble in hot than in cold water. If a saturated solution of such a substance be made in hot

water and then the water be allowed to cool it will, in general, not be able to hold so much of the solid in solution and the excess separates or as it is usually called is deposited in the solid form, often as crystals.

The hot saturated solutions of some bodies do not deposit any of the dissolved substance if the solution is perfectly quiet while cooling and excluded from the air; such solutions are called supersaturated.

Water of Crystallization. Many salts in crystallizing from their aqueous solutions retain in combination a greater or less amount of water called *water of crystallization* for to it the form of the crystal is due. The amount of this water varies with the conditions of crystallization but the water and the salt are always present in molecular proportions by weight. Some salts when exposed to dry air lose their water of crystallization and crumble to a dry powder, this process is termed efflorescence. Those salts which do not part with their water of crystallization in dry air at ordinary temperature, do so at the boiling temperature or at a somewhat higher one.

Salts generally lose their color as well as their crystalline form by the removal of their water of crystallization. Some sympathetic inks owe their use to this property of changing color. A solution of the salt is used as ink but is invisible until the paper used for the writing is warmed; cobalt chloride is such an ink.

Some salts retain a portion of their combined water usually one molecule more tenaciously than their water of crystallization; this is called *water of constitution*. In some cases it can be replaced by a salt.

From the investigations of Guthrie it seems probable that all soluble salts form compounds with water at some temperature. Those salts which combine with water and are soluble only at temperatures below 0° C are called eryo-hydrates.

Many salts which solidify without combined water may enclose some water mechanically; such salts when heated are

likely to fly to pieces with a small report and are said to decrepitate. Bodies which absorb moisture from the air and become damp and ultimately liquid, are said to deliquesce.

The thermal effect of the solution of a solid when there is no chemical effect is cold.

Solution of Liquids. Water dissolves many liquids, some in all proportions. In such event it is usual to say that the liquids mix in all proportions, though the solution may be accompanied by a decided chemical action with a development of heat; water and sulphuric acid are examples. In other cases the solution is confined to certain limiting proportions of the liquids. In case of the solution of solids and liquids a contraction takes place in the volume of the solution, the volume being less than the sum of the volumes of the two bodies.

Solution of Gases. Gases are very generally soluble in water to a greater or less extent and the thermal effect of such solution is opposite to that in the case of solids, heat being produced. The heat is very evident when the gas is very soluble as in the case of ammonia and hydrochloric acid. Gases in most cases are removed from solution by heating, when not thus liberated they form definite compounds with the liquid and distil over with it; the compounds of hydrogen with the halogen elements are examples of this last class of gases. From the facts stated in regard to solutions it will be observed that, like alloys, they differ both from what we have defined as true chemical compounds and also from mere mechanical mixtures; perhaps the most evident distinction is that they differ from true chemical compounds by having no invariable composition, and from mechanical mixtures by the fact that, except in a few cases, there is a limit to the proportions in which the constituents may be present.

Chemical Properties of Water. It has already been stated that oxygen and hydrogen combining to form water develop great heat; we should therefore expect water to be a permanent and stable compound. Although this is a fact, water can be readily decomposed in several ways.

The alkali and alkaline earth metals decompose water at the ordinary temperature; for example, $K_2 + H_2O = K_2O + H_2$.

Some other metals do so at higher temperature. It may also be decomposed by the electric current. At high temperature water is decomposed into its elements, the decomposition according to Deville, beginning about 1000°C . and continuing with the increase of temperature up to about 2500°C . when it is completed. After the decomposition has commenced any fall of temperature will cause a recombination of the elements.

This general decomposition of a substance with increasing temperature accompanied by a disposition of the constituents to combine and reproduce the substance by a reduction of temperature is called *dissociation*.

In its action on vegetable colors, water is neither acid nor basic. It combines with both basic and acid oxides to form definite chemical compounds. Its combinations with the oxides of the alkali and alkaline earth metals develop much heat and result in the compounds called hydroxides; for example, $K_2O + H_2O = 2KOH$, $CaO + H_2O = CaO \cdot H_2$; as already stated it is not believed that water as such exists in these compounds but the oxygen and the hydrogen are present in the form of hydroxyl.

Water combines with the acid oxides to form acids; for example, $H_2O + SO_3 = H_2SO_4$.

Composition of Water. The composition of water may be determined by analysis or by synthesis. The analysis or separation of water into its constituents, may be accomplished by passing an electric current through it under proper conditions. With proper arrangements the con-

stituent gases may be collected and their volumes and weights determined.

The composition by *synthesis* can be determined by causing oxygen and hydrogen to combine directly, as by the passage of the electric spark through a mixture of the gases under such conditions as give the volumes of the gases involved. From the volumes the weights can be computed from the relations of the specific gravities.

The synthetic determination can be more accurately made by causing an unknown quantity of hydrogen to combine with a precisely determined weight of oxygen and then weighing the water produced. The difference between the weight of the water produced and the weight of oxygen employed gives the weight of hydrogen that has combined with the oxygen. This is designated as gravimetric synthesis and a convenient method often pursued is to pass pure dry hydrogen over a known weight of heated copper oxide and accurately weighing the water produced; the loss of weight in the copper oxide gives the weight of the oxygen; the difference between this and the weight of the water produced gives the hydrogen; $\text{CuO} + \text{H}_2 = \text{H}_2\text{O} + \text{Cu}$.

NATURAL WATERS.

Pure water is seldom or never found in nature. The impurities result from the materials, solids, liquids, or gases with which it comes in contact and they may be either in suspension or in solution. Suspended impurities are merely finely divided particles of matter mechanically distributed in the water, and they may be gotten rid of by subsidence or filtration; water often contains no suspended matter. Soluble impurities must be separated by distillation or a combination of this with more purely chemical means.

The natural waters may be classified according to their occurrence as rain, sea, river, spring and well waters.

Rain Water. Rain is the purest form of natural water but even it contains gaseous and dust particles derived from

the atmosphere through which it passes. The gases dissolved by falling rain are of course those present in the atmosphere. Rain water accordingly always contains oxygen and nitrogen and generally more or less ammonia and carbon dioxide and often traces of other gases the quantity depending upon local conditions.

By boiling rain or other natural water the gases in solution are driven out and may be collected. It is thus found that the oxygen and nitrogen in solution in these waters are not in the same proportion as they exist in the air. This is one of the best proofs that air is a mixture of oxygen and nitrogen and not a chemical compound.

Spring and Well Water. The rain and the water resulting from the melting of snow, sleet, and hail flow over the surface of the earth on their way to the sea. When these waters sink below the surface and reappear, they constitute springs; if their subterranean channels be tapped artificially we have wells. Spring and well waters, in addition to the impurities of rain water, dissolve many soluble substances encountered in their flow; the impurities in such water depending upon the rock material through which they pass.

The most common and abundant impurities are the carbonates and sulphates of the alkaline earth metals, the chlorides and sulphates of the alkali metals, silica (silicon oxide), carbon dioxide, and hydrogen sulphide.

Many other substances of less frequent occurrence and of less importance are found naturally in these waters.

By contamination from artificial sources, as by city or town sewage, etc., spring and well, and even river waters may become very impure and entirely unfit for human consumption. It is believed that zymotic diseases generally, and it is known that two of them, cholera and typhoid fever, are frequently propagated by drinking-water. The infectious or zymotic matter is contained in the discharges of affected people and passes by defective drainage into sources of water supply. In cases of such artificial contamination the additional impurities in the water are salts of nitrous and nitric acids, ammonia, and chlorides. By chemical analysis and a consideration of the sources of a water

supply, its safety for drinking purposes can generally be determined, but any water contaminated by sewage should be classified as dangerous.

Hard and Soft Water. Common waters have been roughly classified as hard and soft, a classification originally depending upon their action upon soap. Soap when rubbed in soft water forms a lather much quicker than when hard water is used. With the latter white curdy flakes not observed with the soft water, make their appearance before a lather is formed; this action is due to chemical causes and will be presently explained.

The hardness of water is mainly due to the presence in the water of the *carbonates* and *sulphates* of *calcium* and *magnesium*. The carbonates of the metals, except those of the alkalies, are not soluble in pure water but if the water contains carbon dioxide in solution, as natural waters generally do, they will dissolve the carbonates.

Magnesium sulphate is readily soluble in water and calcium sulphate very slightly so.

The hardness due to the carbonates in solution is termed *temporary* because it can be readily removed; that due to the sulphates is called *permanent* because of the difficulty of removing it.

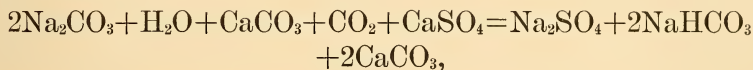
Since the temporary hardness brought about by the carbonates in solution is due to the presence of carbon dioxide, if this be removed the carbonates will be precipitated. The carbon dioxide may be driven off by boiling, on account of its decreased solubility with increase of temperature, and the carbonates will deposit on the sides of the containing vessel.

Calcium sulphate is very slightly soluble in cold water and less soluble at high temperature. By evaporation of the water and increase of temperature there would also be deposited some calcium sulphate, but the calcium sulphate can not be entirely removed by boiling alone.

These depositions explain the furring of kettles and incrustations of boilers. These deposits are usually colored brown or red due to the presence of iron oxide and vegetable matter, the former resulting from the iron carbonate deposited from the water.

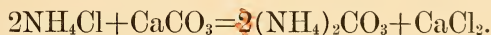
The temporary hardness of the water may also be removed by adding to the water a solution of calcium hydroxide, which combines with the free carbon dioxide removing it as calcium carbonate and causing the deposition of the dissolved carbonate, $\text{H}_2\text{O} + \text{CaCO}_3 + \text{CO}_2 + \text{CaO}_2\text{H}_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O}$; this is the principle of the Clark process for softening water.

Both the temporary and permanent hardness are removed by the household process of adding an alkaline carbonate to the waters,



but this is practicable only on a small scale.

It is often desirable to prevent the incrustation in boilers and the most efficient means yet suggested is to add ammonium chloride to the waters employed—there are then formed ammonium carbonate and calcium chloride, the latter remains in solution in the water and the former volatilizes in the steam,



The incrustations formed in boilers fed with sea water are mainly due to calcium sulphate and magnesium chloride in sea water.

Natural Deposits from Hard Water. The metallic carbonates except those of the alkalies are insoluble or nearly so in pure water, but they dissolve in water containing carbon dioxide and the greater the amount of carbon dioxide the greater the amount of the carbonates dissolved.

Subterranean waters are often heavily charged with

carbon dioxide and coming in contact with limestone rocks they dissolve much calcium carbonate. When these waters come to the surface of the earth the carbon dioxide escapes, due to diminished pressure, and the dissolved carbonates are deposited.

This explains the phenomena observed at the so-called petrifying springs which are constantly depositing limestone, and will rapidly cover with it any body placed in their waters. This phenomenon is abundantly witnessed in the Yellowstone Park—the objects are merely coated and not petrified.

Such waters trickling into caves often deposit their salts so as to form large columns, often of great beauty, called stalactites and stalagmites.

Of course when waters containing salts in solution are evaporated, they then leave their salts behind, so that deposits may occur by evaporation of the water as well as by the removal of the carbon dioxide.

It is possible that the solution of the carbonates generally by carbon dioxide in solution, may be due to the formation of acid carbonates of the metals, but the formation of these substances has not been proved and if they are formed they are easily decomposed, for as we have seen boiling drives off the carbon dioxide; if this is the case the soluble carbonate of calcium is represented thus—



Action on Soap. To understand the action of hard water on soap it is necessary to know that soap is itself a metallic salt of an alkali metal and fatty acid and common soap may be represented by the formula NaFt in which Ft stands for the complex formula of the fatty acid radical. When these soaps are treated with hard waters the calcium and magnesium salts by double decomposition form the soaps of these metals which are insoluble and perceptible as curdy scum on the water. A true lather from the soap will not form until the salts to which the hardness is due are removed by the formation of these insoluble soaps.

River and Sea Waters. River water does not differ essentially from well and spring water. The quantity of both mineral and organic impurities being diminished by the conditions of continual motion and exposure to the air.

Sea water contains the same salts as spring and river waters and in addition a large amount of common salt, about four-fifths of the saline constituents of sea water being sodium chloride. The compounds of bromine and iodine are also found in small quantities in sea water. A gallon of sea water usually contains about 2500 grains of mineral salts. Sea water has no point of maximum density above the freezing point and solidifies at -2°C .

Mineral Waters. Natural mineral waters are those spring waters which contain mineral substances in such quantity as to exert a medicinal effect on the animal system or as to render them entirely unfit for drinking purposes. Mineral and medicinal springs are very widely distributed; some of the common kinds are chalybeate springs, which contain some salt of iron in solution; saline springs which contain one or more of a large number of mineral salts; carbonated springs which contain carbon dioxide in solution; hepatic springs which contain hydrogen sulphide in solution. The escape of the gaseous constituents often produce effervescence; the same spring often contains both solid and gaseous constituents.

Purification of Water. Waters often become purer by natural processes. This is the case with running waters and especially when they are subjected to thorough agitation and exposure to the air; an unfit water may thus become fit for drinking in a purely natural manner. The purity of all turbid water is greatly increased by allowing it to stand in tanks or reservoirs, by which most of the suspended matter is deposited. After remaining for some time in storage reservoirs it is customary to filter all large water supplies. The most

common method adopted is to allow the water to flow through layers of sand of different degrees of coarseness. Sand filtration when properly carried on is very efficient in removing all suspended impurities, but it has little influence on the dissolved matter. It is also claimed by Professors Koch and Frankland that sand filtration removes a very large per cent of microscopic organisms. Besides sand, filters of charcoal or of coke and sand have been employed for purification on a large scale.

The Hyatt filter which is largely used in this country uses coke and sand, in this process a little alum is added to the water before filtration.

Filters of finely divided iron have been used in Antwerp in case of very impure water; these filters exert a chemical as well as a mechanical effect upon the water. There are many other methods of purifying drinking water on a small scale. For refined chemical purposes water is purified by distillation.

Alum is frequently used to clarify water; the effect is probably mainly due to the fact that if there be any carbonates in solution in the water, the alumina is precipitated, which has a coagulating effect and carries suspended matter with it.

HYDROGEN PEROXIDE— H_2O_2 .

This substance has the composition H_2O_2 . It was discovered in 1818. It is a great oxydizing agent in the case of many substances, readily giving up half its oxygen and being converted into water; upon other substances it acts as a reducing agent, being itself converted into water and oxygen liberated; it thus acts upon ozone— $\text{O}_3 + \text{H}_2\text{O}_2 = 2\text{O}_2 + \text{H}_2\text{O}$.

Hydrogen peroxide is a colorless, transparent, syrupy liquid; it is heavier than water, has a bitter taste, and mingles with water in all proportions.

Its most useful applications in the arts are by virtue of its oxidizing power.

Paintings which have blackened due to the formation of lead sulphide can be restored to their original color by washing with a dilute solution of hydrogen peroxide—the lead being converted into lead sulphate. It is very important to the student of chemical philosophy because of its chemical relations.

CARBON.

Carbon occurs free in nature in three distinct allotropic forms—as diamond, graphite, and mineral coal. These three forms differ widely in appearance and physical properties, but their chemical relations prove their identity. The first two are crystallized and very nearly pure carbon; the third is amorphous, uncrystallized and includes many varieties of coal differing greatly in purity—the three principal varieties are anthracite or hard coal, bituminous or soft coal, and lignite or brown coal.

In combination carbon is widely distributed. It exists in combination with oxygen in the carbon dioxide of the air, is present in all mineral carbonates, and is a constituent of all organic substances. It is the element by virtue of which all organic substances turn black when heated with limited access of air. All forms of carbon are solid, insoluble in all ordinary solvents, fused iron being the only known solvent, non-volatile except at the high temperature of the electric arc.

Diamond. This is one of the rarest of substances and one of the most precious gems. It is usually obtained from alluvial washings and appears generally to have come from sandstone or quartzite rock; nothing definite, however, is known as to its original formation.

It crystallizes in forms derived from the octahedron and is the hardest substance known. For use in jewelry it is cut and polished so as to bring out the brilliancy of its faces. Besides its use in jewelry it is used for pointing drills for boring in hard rock, to cut glass, and its dust is used in polishing.

If heated very highly out of contact with air, as by the electric arc, it is converted into a black mass resembling graphite, but without loss of weight. It can be burned in the air and then leaves a small quantity of ash. Recently diamond, or carbon crystallized with the lustre of diamond,

has been prepared artificially, but the crystals thus made were very small.

Graphite. This is found in beds and veins in the oldest crystalline rocks, has a greyish black color and metallic lustre, and is so soft as to leave a mark when rubbed on paper.

It is a very useful substance, being employed in making the so-called lead pencils, for covering iron to prevent rust, and for mixing with clay to make crucibles which are designed to stand high and sudden change of temperature. Graphite is often produced artificially in the cooling of molten cast iron. It is also used as a reducing agent in some metallurgic operations.

AMORPHOUS CARBON.

This term includes in addition to the native mineral coals all the common artificial forms of carbon. The mineral coals are fully described in mineralogy. The principal artificial varieties of amorphous carbon are charcoal, lampblack, animal charcoal and coke. Lampblack is the form of carbon which is often deposited upon cold objects by the flame of gas or burning oil. These combustible bodies are composed almost entirely of carbon and hydrogen, and if the flame could be cooled down or the supply of air limited, the carbon escapes combustion and is deposited in a finely divided state commonly called soot.

Lamp-Black is manufactured by subjecting organic substances rich in carbon to imperfect combustion; that is combustion with an insufficient supply of air. For this purpose oils, fats, resins, and tarry matters are burned with a limited supply of air and the products of combustion conducted through a flue into a large chamber, along the sides and from the ceiling of which are suspended large cloths upon which the unburned carbon is deposited. The lamp-black thus obtained usually contains resinous or oily

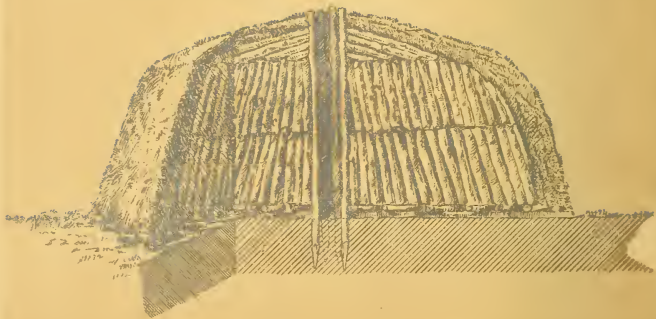


FIG. 4.
Preparation of Charcoal.

substances and other impurities depending upon the organic body burned. It is however sufficiently pure for the purposes for which it is generally used; viz., printers' ink and black pigments.

Charcoal. Charcoal is the form of carbon obtained by heating wood out of contact with air. If wood be heated in the air it is entirely consumed except a small quantity of ash which is composed of the incombustible mineral matter of the wood. The part that has disappeared, the sap and the woody fibre, are composed almost entirely of carbon, hydrogen, and oxygen. The woody fibre (cellulose) which constitutes nearly the entire solid part of the wood is more than one half carbon the remainder being oxygen and hydrogen.

If wood be heated to redness out of contact with the air, no combustion can occur, but under this temperature the constituent elements of the wood rearrange themselves into simpler and more stable compounds. In this change the carbon is mainly left, retaining the form of the wood, but largely diminished in volume and still more so in weight.

This resolution of a complex substance into simpler and more stable forms under the influence of high temperature out of contact with air is termed destructive distillation.

In the case of wood it is often called charring, coaling, or carbonizing.

The earliest and still the most common way of preparing charcoal for fuel, is as follows:

Preparation of Charcoal. Billets of wood are built into a mound or stock around an upright pole or bundle of brush-wood which is withdrawn after the stock is completed and leaves an opening called the chimney. The billets may be nearly vertical, or horizontal, or inclined at any angle. When completed the mound usually has a dome shape and may have a diameter varying from thirty to fifty feet and with a height from ten to fifteen feet. The finished heap is

covered with chips, leaves, soil and earth, and often the coal dust of a previous burning is used for this purpose. Numerous openings are left around the base of the mound for the admission of air and escape of the products of distillation.

The kiln is kindled in the centre and after the fire is started the top is closed. More air is required in the early stages of the carbonization so that the openings at the bottom are gradually closed and the mound is left to smoulder and cool. By this process the weight of charcoal obtained never exceeds 25% of the wood used. In this country as in many other places kilns or charcoal ovens are often built of brick or masonry; they are generally rectangular with arched tops or of a bee-hive shape. In these ovens the destructive distillation is accomplished by the combustion of a certain portion of the wood of the heap. In this country there is claimed for such ovens an economy of time and a gain in the quantity and quality of the charcoal but these advantages are denied at other places—the ovens are sometimes arranged to collect the products of distillation.

Charcoal is also made by the destructive distillation of the wood in cast iron retorts, the wood being placed in a perforated iron case within the retort. In this method the heat is obtained from other fuel than the wood itself, though sometimes the combustible products from the wood are led to and burned in the furnace beneath the retort. At other times these products are condensed and used in the preparation of acetic acid, wood naphtha, and methyl-alcohol.

Distillation in retorts yields a greater per cent of charcoal and of better quality than the methods first described.

All forms of carbon thus obtained contain impurities due to the non-combustible and non-volatile mineral matter of the wood.

Properties and Uses of Charcoal. The appearance of charcoal needs no mention. It is one of the most unchanging solids known under ordinary conditions. This property

of carbon has long been recognized and is shown in the charring of wood intended to withstand extended exposure. Oak staves planted in the bed of the Thames by the ancient Britons in their defensive works against Cæsar were charred and thus have been perfectly preserved to the present day. Charred stakes for marking the limiting lines of estates are often used.

Charcoal is very porous and due to this property exerts an absorbent action on many substances. Oxygen is absorbed by it in considerable quantity and many other gases to a far greater degree. This is especially noticeable with those gases which can be readily liquefied. It absorbs under ordinary conditions fifty times its volume of hydrogen sulphide and twice that amount of ammonia. A gas thus absorbed if capable of oxidation will be acted upon by the oxygen also contained in the charcoal. This property of charcoal explains its frequent use in deodorizing offensive matter and in purifying offensive atmosphere.

Ammonia and hydrogen sulphide are two of the most common products of putrefaction and both are readily absorbed by charcoal.

The absorbing power of charcoal also extends to liquids and solids, it is accordingly used to make water filters.

Water passed through a good charcoal filter is clear and odorless. It is especially efficient in removing coloring matter. The charcoal has to be periodically heated to retain its absorbent powers.

Besides the above uses charcoal is largely employed as a fuel and in the manufacture of gun-powder.

With a free supply of air it burns readily without flame, producing carbon dioxide and yielding about twice as much available heat as an equal weight of wood. One pound of carbon burned to carbon dioxide will produce 8080 units of heat, C. scale. Its use in the manufacture of gun-powder will be referred to under that subject.

Animal Charcoal. This form of carbon is made by the destructive distillation of animal substances as bone, skin, blood, &c., commonly from the first named substance. Bones are composed approximately of one-third animal matter and two-thirds mineral matter, three-fourths of this mineral matter being calcium phosphate. The animal matter is composed mainly of carbon, hydrogen, oxygen, and nitrogen. The result of the destructive distillation of bones is a charred mass consisting of about one-tenth carbon and nine-tenths mineral matter.

The decolorizing power of this form of charcoal far exceeds that of other forms and it has frequent technical application for this purpose and is used industrially in sugar refineries and distilleries.

The products from the distillation of bones are often collected and used, and the mineral matter from the bone-black itself is eventually employed as a fertilizer.

Coke. Common coke results from the destructive distillation of soft or bituminous coal. This distillation is sometimes made by burning coal in heaps as in the conversion of wood into charcoal, but generally the coke is prepared in specially constructed ovens and of these there are many forms. They are constructed of suitable masonry lined with fire-brick. In some of these the heat for the distillation is obtained by burning part of the coal in the oven; in others the heat is obtained without burning any of the coal in the oven. In the latter kind the combustible gases driven from the coke and other fuel are burned to supply heat. The forms of coke ovens are too numerous for description here, the object in all cases is to accomplish the distillation with as little consumption of fuel as possible.

The ovens are also varied in construction, depending upon whether they are arranged to secure the tar and ammonia. In this country the coke is usually made in bee-hive ovens and the secondary products are not saved. In Europe

the retort-ovens are very generally employed, and, in certain localities, the by-products from the volatile constituents of the coal equal in value the coke produced. The coke contains in addition to the fixed carbon the incombustible ash of the coal.

Coke is of a dark grey color with a slightly graphitic lustre; it produces a much higher temperature than common coal and is much used in iron smelting and other metallurgic operations.

Coke is always produced in the manufacture of coal gas, the coal in the operation being distilled in closed iron retorts. In this manipulation it often happens that some of the denser gases containing carbon and hydrogen driven from the coal are decomposed by the high temperature and the carbon deposited upon the sides of the retort and is known as gas-coke. It is used for plates in carbon batteries and also for the manufacture of carbon rods for electric arc lights.

Chemical Properties of Carbon. Carbon at the ordinary temperature is an inactive element, not combining with any other element; at higher temperature it combines directly with sulphur, hydrogen, and oxygen and under proper conditions will combine with other elements; at elevated temperature it is especially active in combining with oxygen. Heated to redness it burns brilliantly in pure oxygen and by the aid of heat it abstracts oxygen from many oxides removing and combining with the whole or a part of their oxygen.

When burned with a full supply of air carbon always yields carbon dioxide; with a limited supply, carbon monoxide is produced. In case an oxide gives up its oxygen at a low temperature to carbon, carbon dioxide is formed, but if a high temperature is required carbon monoxide is produced; these actions are represented by the accompanying ~~re-~~
~~actions~~;

Equations



This removal of oxygen from a body has already been defined as a reduction, hence carbon is a reducing agent. It is the most important reducing agent employed in the industrial arts and upon this property and its heat giving power depend its uses in metallurgic operations.

COMPOUNDS OF CARBON AND OXYGEN.

CARBON DIOXIDE.

There are known two compounds of carbon and oxygen, carbon monoxide and carbon dioxide, both of which are gaseous at ordinary temperature. The latter is the more important; it has already been stated that it is a constituent of the atmosphere, being normally present in the proportion of from three to four volumes in 10000 of the air. Its constant occurrence in the air is readily understood from known considerations.

It is the product of the combustion of any form of carbon or any compound of carbon in a full supply of air. As all common fuels are composed mainly of carbon or its compounds it may be said that carbon dioxide is an abundant product of all ordinary combustion.

It is likewise given off in all animal respiration, the oxygen of the air which is inspired combining with the carbon of the system to form carbon dioxide which is exhaled.

All living vegetation extracts carbon dioxide from the air, but when the plant dies the process of decomposition in the course of time restores the carbon dioxide to the air again. If the plant is devoured by animals or consumed for fuel its carbon eventually returns to the air as carbon dioxide.

Carbon dioxide is also given off to the air during the processes of fermentation and putrefaction of organic substances.

It is present to a greater or less extent in all spring waters and in some places, especially in volcanic regions it

escapes rapidly from such waters when they come to the surface, giving effervescing springs. It often issues in considerable quantity from openings in the earth's crust. When coming from such openings or even from springs it sometimes accumulates in neighboring depressions in such quantity as to destroy the life of animals venturing into them. Such a poison depression has been found at the east side of the Yellowstone Park; the poison valley of Java is another and the accumulation of gas around the soda springs (so called) in south eastern Idaho often causes the death of birds seeking water.

The air which permeates soils is found to be richer in carbon dioxide than is atmospheric air.

In the combined form carbon dioxide occurs as a constituent of all limestones and other carbonates and consequently exists in this form in enormous quantity. It constitutes over 96 per cent of oyster shells and egg shells.

Physical Properties of Carbon Dioxide. Carbon dioxide at ordinary temperature is a colorless gas, and has a slightly acid taste and smell. Its formula shows it to be much heavier than air and its greater density explains its disposition to seek the lower levels. At 14° C. water dissolves its own volume of carbon dioxide and the quantity dissolved is directly proportional to the pressure to which the gas is subjected. When the pressure is diminished or removed the amount dissolved is diminished and if there is much diminution of pressure the gas escapes with effervescence.

Carbon dioxide can be liquefied without very great difficulty to a mobile colorless liquid which will not mix with water. Its boiling point in the liquid state is -88° C. (much of the liquid carbon dioxide is now manufactured for use as a fire-extinguisher). By causing it to evaporate under an air pump its temperature is lowered to -130° C. Like many other bodies which are liquefied only by very great pressure its coefficient of expansion is very great, being greater than the coefficient for gases.

Chemical Properties of Carbon Dioxide. Carbon dioxide is not combustible as it can not take up more oxygen. It will not support ordinary combustion and will extinguish flame; a few bodies which have a great affinity for oxygen will burn in carbon dioxide. If potassium be ignited and then dipped into a jar of carbon dioxide it will continue to burn. Air which contains less than 3 per cent by volume of carbon dioxide will extinguish a taper—that is when the carbon dioxide is about one-eighth the volume of the oxygen. Carbon dioxide is not poisonous when taken into the stomach but it will not support respiration. It is not poisonous in this case, but merely suffocates by depriving of the necessary amount of oxygen and also prevents the escape of the carbon dioxide from the system.

A taper burning in a confined space is extinguished as soon as the carbon dioxide reaches a certain amount and long before all the oxygen is exhausted. Similarly confined air becomes unfit to breathe long before the oxygen is exhausted. Any considerable amount of carbon dioxide above the normal in air to be respired is objectionable in that it diminishes the proportion of oxygen. The actual amount of pure carbon dioxide that must be present in the air to render it unfit for respiration is not definitely settled. It has been found that air containing as much as 5 per cent may be breathed without injury and recent experiments indicate that a much larger proportion of *pure* carbon dioxide may be breathed for several hours without ill effect.

It has been shown that the bad effects experienced in poorly ventilated rooms are due to other waste products, than carbon dioxide, given off from the lungs during respiration. Besides the carbon dioxide, water vapor, nitrogen, and oxygen of the expired air, there are other organic substances undergoing decomposition which have a poisonous action in the system and to these are to be largely attributed the unwholesome conditions so rapidly developed in

overcrowded and poorly ventilated rooms. As carbon dioxide is constantly given off in respiration along with other organic impurities the amount of the first in the air will indicate approximately the quantity of the latter and therefore may be taken as a test of the fitness of the air for respiration.

Generally speaking it may be stated that when the volume of the carbon dioxide is over $\frac{1}{1000}$ the volume of the air it should not be breathed for any considerable time; when the volume of the carbon dioxide reaches $\frac{1}{200}$ the volume of the air, its effects soon become perceptible in languor and disagreeable sensations and any amount above this is very deleterious; when the amount has reached three per cent it has been known to produce death.

A well, fermenting tun, or any confined space where this gas is suspected, should be tested before entering it. If a candle flame is made dim by the air the space should be considered unsafe. When any person is quickly overcome by such an atmosphere another person can not safely go to the rescue without first increasing the proportion of oxygen to the carbon dioxide. This may often be quickly done by moving an open umbrella, a bundle of straw or of brush up and down through the space.

The above described properties of carbon dioxide make evident the necessity for good ventilation. The amount of carbon dioxide given off from the lungs and skin amounts to about $\frac{7}{10}$ cubic feet per hour, an ordinary three-foot gas burner gives off about two and one-half times that amount. In order that the added carbon dioxide shall be distributed through the proper amount of air to fit it for respiration, it is evident that a large amount of fresh air must be introduced into constantly occupied rooms. It is of course easy to compute this amount under any given conditions. In general it may be stated that perfect ventilation should be prepared to supply one thousand cubic feet of air per man

per hour, though one half that amount is usually considered good ventilation.

Preparation of Carbon Dioxide. Carbon dioxide is invariably produced when carbon is burned in a full supply of oxygen; for example, $C + O_2 = CO_2$; from this source it always contains other substances.

It is readily prepared for laboratory purposes by acting upon fragments of marble ($CaCO_3$) with dilute hydrochloric acid. The carbon dioxide escapes with effervescence and is usually collected by downward displacement as it is somewhat soluble in water. The apparatus described for making hydrogen may be used in this case. The action is represented thus, $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$.

Any of the other mineral acids will liberate carbon dioxide from a carbonate, so that it can be readily prepared in many ways.

Carbon dioxide is largely used in the manufacture of artificial mineral waters.

Carbonic Acid and Its Salts. An aqueous solution of carbon dioxide exhibits weak acid properties. It colors blue litmus red, but the blue color returns upon drying. The solution acts upon bases and forms the salts called carbonates. The formulæ of the carbonates indicate the existence of an acid having the formula H_2CO_3 though this substance has not been isolated. It is probable that the acid is formed whenever carbon dioxide is passed into aqueous solution, but it readily breaks up into carbon dioxide and water. On account of the similarity of the carbonates to other salts, they are universally considered as formed by the replacement of hydrogen in carbonic acid by metals and the acid is bibasic.

The carbonates are a very important class of bodies and it may be well to repeat their properties. The carbonates are all decomposed by mineral acids, are all, with un-

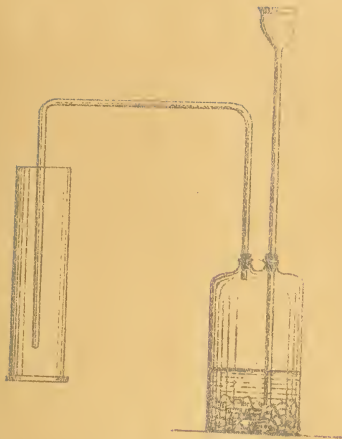


FIG. 5.
Carbon Dioxide by Displacement

important exceptions, insoluble in water except the carbonates of the alkalis, and are all decomposed by heat except those of the alkalis. They are all soluble in water containing carbon dioxide.

CARBON MONOXIDE.

Physical Properties. Carbon monoxide is a colorless, tasteless gas with a very faint smell; it is slightly lighter than air as may be seen from its formula. It is almost insoluble in water. Its critical temperature is about -140°C .

Chemical Properties. Carbon monoxide is an extremely poisonous gas. It acts upon the red corpuscles of the blood and deprives the blood of its power of distributing oxygen to the system. It forms an explosive mixture with one half its volume of oxygen. It burns in air with a pale blue flame producing carbon dioxide, but extinguishes ordinary flame. At high temperature it readily takes oxygen and forms carbon dioxide; for this reason it is a powerful reducing agent removing oxygen from many metallic oxides and reducing them to the metallic state. It is accordingly a very valuable agent in many metallurgic operations. Its union with oxygen gives out much heat; carbon monoxide burning to carbon dioxide gives more than two-thirds of all the heat produced by the complete combustion of the carbon to carbon dioxide.

Production and Uses. Carbon monoxide is always produced by the incomplete combustion of carbon or carbonaceous substances, that is when these are burned with an incomplete supply of air.

If carbon dioxide be passed over heated charcoal or other carbon it gives up one half its oxygen to the carbon, both being converted into carbon monoxide, as indicated by the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$.

This action explains the phenomenon frequently observed in connection with an open anthracite coal fire when a pale

blue flame is seen to play over the top of the mass of coal; the combustion of the coal in the lower part of the grate with full supply of oxygen produces carbon dioxide, this passing through the heated layers of coal above, is converted into carbon monoxide. This carbon monoxide upon reaching the upper surface of the coal comes in contact with the air and burns with the blue flame observed.

This ready production of carbon monoxide is often made use of in metallurgic operations when it is desired to have a flame play over the surface of an ore placed on the hearth of a reverberatory furnace.

Anthracite coal which burns with but little flame is frequently employed in such furnaces and it then becomes necessary to heap the coal in the grate so as to form a mass of considerable height. The carbon monoxide is produced precisely as described above in the grate and passes into the furnace chamber and when air is admitted the carbon monoxide burns with a flame. By properly regulating the supply of air a high temperature can be produced.

The attraction which carbon monoxide has for oxygen at a high temperature enables it to remove this element from many of its compounds. Carbon monoxide is accordingly one of the most powerful reducing agents and, as will be subsequently seen, the property is generally turned to account in removing oxygen from the metallic oxides, reducing the oxides of the metals.

Carbon monoxide is one of the essential elements of water-gas, hydrogen being the other; carbon dioxide and nitrogen are also present in limited quantities. This water gas is now largely used for illuminating and for other purposes.

Water gas is prepared by passing steam over white-hot coke, the result is indicated by the reaction $C + H_2O = CO + H_2$.

Some carbon dioxide is also present for the reason that at lower temperature the action of steam on carbon is to produce carbon dioxide; at certain temperature steam also acts

slightly on carbon monoxide producing carbon dioxide. Water gas usually consists of about 30% of hydrogen and 40% of carbon monoxide the remainder being nitrogen and carbon dioxide.

As both hydrogen and carbon monoxide burn with faintly luminous flames, the gas to be used as an illuminant must be enriched or carburetted. This is accomplished by admitting naphtha or crude oil to the heated coke during the gas production or by passing the gas through naphtha or over liquefied naphthalene.

Water gas is valuable as a heat producer and then does not need to be carburetted. Its flame is entirely free from smoke and comparatively so from sulphur compounds. It produces a high temperature and a clear heat and is very valuable in melting and welding metals and in porcelain and glass manufacture.

For laboratory purposes carbon monoxide is readily obtained by heating potassium ferrocyanide with dilute sulphuric acid.

COMPOUNDS OF CARBON AND HYDROGEN.

Carbon and hydrogen form a larger number of compounds than any other two elements. These compounds are designated as hydrocarbons. They enter largely into the composition of nearly all combustible bodies and include many of the inflammable gases, naphtha, benzene, &c.

It is probable that all hydrocarbons are primarily derived from the organic kingdom and the study of these compounds belongs to organic chemistry. Only three of the simple hydrocarbons will be mentioned here; they are all constituents of common coal gas.

METHANE; MARSH GAS; CH_4 .

Methane is the only hydrocarbon containing one atom of carbon. It is found abundantly in the free state in nature. It is frequently termed marsh gas from its occurrence in marshy places. The bubbles of gas which rise to the surface

when the mud at the bottom of stagnant pools is disturbed, are in fact marsh gas. It is believed to be one of the products of the decomposition of vegetable matter during its conversion into coal, hence its frequent occurrence in coal mines, where it is known as fire-damp. It is probable that all the hydrocarbons of petroleum and similar oils generally are derived in the same way.

Physical and Chemical Properties. Methane is a colorless, odorless, and tasteless gas. Its formula shows it to be much lighter than air, hence it diffuses and mixes rapidly with it. When mixed with oxygen or air in suitable proportions it explodes violently upon ignition. The most violent explosion is indicated by the reaction, $\text{CH}_4 + \text{O}_4 = \text{CO}_2 + 2\text{H}_2\text{O}$, in which there is just enough oxygen to completely oxidize the carbon and hydrogen. The relative volumes of marsh gas and oxygen for this action are shown in the equation to be two volumes of oxygen to one of marsh gas; it would accordingly require ten volumes of air for the complete oxidation of one volume of marsh gas.

It is marsh gas which so frequently gives rise to the fatal explosions in coal mines. It will be observed that the products of the explosion are also irrespirable and constitute the after-damp of mine explosions.

Marsh gas has not been prepared by the direct union of its elements but can be prepared artificially. Marsh gas does not unite with other bodies without decomposition; chlorine decomposes it in direct sunlight, atoms of chlorine successively replacing atoms of hydrogen. At a high temperature marsh gas is separated into carbon and hydrogen.

ACETYLENE; ETHENE; C_2H_2 .

Acetylene can be produced directly from its elements by highly heating carbon in an atmosphere of hydrogen. This may be accomplished by immersing the electrodes of a voltaic arc in an atmosphere of hydrogen. The operation

is of but little practical importance but it is of great theoretical interest because it is the first step in the artificial production of a large number of organic compounds.

Physical and Chemical Properties. Acetylene is a colorless gas having a faint odor of geranium. From an ordinary gas jet it burns with a smoky flame, but when the air and gas are properly apportioned its flame is brilliantly luminous. It inflames spontaneously when brought into contact with chlorine and when mingled with air gives a mixture that can be exploded by ignition.

Preparation of Acetylene. Acetylene is now prepared on a large scale by heating lime with powdered coal or other carbon in an electric furnace, by which calcium carbide is prepared. The calcium carbide if immersed in water yields lime and acetylene by this reaction, $\text{CaC}_2 + \text{H}_2\text{O} = \text{CaO} + \text{C}_2\text{H}_2$.

This method of preparing acetylene promises to give it a brilliant future as an illuminant for which purpose it is admirably adapted because of its great light giving power in proportion to the heat and objectionable products resulting from combustion.

OLEFIANT GAS; ETHYLENE; C_2H_4 .

Olefiant gas like the other two hydrocarbons just described is a product of the destructive distillation of coal. It may be obtained artificially by the action of sulphuric acid upon alcohol. It is a colorless gas with a somewhat ethereal odor. It burns with a luminous flame and for complete combustion one volume of the gas requires three volumes of oxygen, $\text{C}_2\text{H}_4 + \text{O}_3 = 2\text{CO}_2 + 2\text{H}_2\text{O}$.

The mixture of olefiant gas and oxygen in this proportion explodes with violence when ignited.

The gas unites with chlorine and bromine, forming oily liquids, hence the term olefiant (oil-making). This action may be applied to determine the amount of the ethylene in the coal gas.

When subjected to high temperature olefiant gas is decomposed with a deposit of carbon and a separation of hydrogen, marsh gas, and acetylene.

CUMBUSTION AND FLAME.

Combustion. The hydrocarbons above described, either separately or together, are found in many of our common inflammable gases; combustion and the properties of flame are accordingly very naturally taken up here.

Combustion in general may be defined as chemical action accompanied by heat and light. The term combustion ordinarily applies to the chemical combination of the oxygen of the air with the body burned.

The temperature to which a body must be raised in order that combustion may take place is called the *igniting point*.

When a body is said to be combustible it is generally meant that it burns in air. It is also customary to regard one of the bodies taking part in the action as the combustible and the other as the supporter of the combustion. The enveloping medium is usually taken as the supporter of combustion and the other as the combustible, so that in the ordinary cases air is the supporter of combustion. These limitations are without scientific basis and the supporter of combustion may be any medium in which the phenomenon will occur.

The process with proper arrangements, when both the bodies taking part in the combustion are gases, is reversible so that the supporter of combustion may become the combustible and the reverse;—thus while we usually burn hydrogen in oxygen, oxygen may be burned in hydrogen. Similarly air may be burned in coal gas and the reverse.

Flame. When both substances taking part in the combustion are gases, the action results in flame, which may be defined as gaseous matter heated to a temperature at which it becomes visible. Solids which do not volatilize at the tem-

perature of combustion do not give flame; carbon and iron are familiar examples.

Luminosity of Flame. This may be due either to the incandescence of gaseous matter or of solid particles present in the flame. A high temperature is always essential to incandescence and consequently to luminosity. In all ordinary flames the gaseous matter which is heated results from the flame-gases themselves; the solid matter may result from these gases or may consist of foreign matter introduced for the purpose.

It has been found as a general rule that denser gases and vapors when heated give off light at lower temperature than the less dense, and heated solids emit light at lower temperatures than gases.

Luminosity without Solid Particles. Examples of combustible bodies which afford dense flames and bright light without solid particles are seen in the case of phosphorus, arsenic, and carbon disulphide, which when burned in oxygen produce highly luminous flames, though all the products of combustion are gases at the temperature. The luminosity of the flame does not depend entirely upon the vapor density of the constituent gases themselves, but are affected by the pressure to which these gases are subjected.

The luminosity of flame may often be increased by increasing the pressure of the medium surrounding the flame.

Thus ~~the luminosity of~~ the flame of carbon monoxide burning in oxygen at ordinary pressure is only moderately luminous, but may be greatly increased by doubling the pressure. The faintly luminous flame of hydrogen burning in oxygen may be greatly brightened by increasing the pressure of the oxygen. For this reason a candle burns more brightly at a low than a high elevation.

Flame Containing Solid Matter. The light-giving power of many of the common illuminating gases is still further

increased by the presence of solid matter intentionally introduced into the flame or separated from the flame-gases during the chemical action of combustion. The Welsbach burner, among common gas-burners, is an illustration of free foreign solid matter introduced into the flame. The great luminosity in this burner is due to the introduction into the flame of a gauze hood of certain infusible metallic oxides.

In the candle, oil lamp, simple gas-flames, and common flames generally, the light is mainly produced by the incandescence of solid carbon particles which are separated in a finely divided state from the flame-gases. There are also usually present or produced in these flames dense hydrocarbons which emit light. The influence of such solid particles may be illustrated by blowing powdered charcoal across a hydrogen flame.

The calcium or lime-light owes its luminosity to a fragment of lime very highly heated by the oxyhydrogen flame.

It is seen from the above considerations that the most essential conditions for luminosity in a flame are—(1) high temperature and vapors which are of themselves dense or made dense under the conditions of burning, (2) highly heated solid particles; the influences of these conditions operate simultaneously in most common illuminating flames.

Structure of Flame. The simple flame is one that results from the combustion of a substance that undergoes no decomposition, but combines directly with the supporter of the combustion—hydrogen and carbon monoxide burning in oxygen are illustrations. There is but a single product of combustion in such cases. All such flames when the gas issues from a circular jet consist of a conical sheath of flame surrounding a cone of the gas. The flame-cone is hollow, that is to say, the interior cone of the gas is not burning. This fact may be simply proved by quickly depressing a white sheet of paper into the flame, when the flame cone will

char an annular space while the interior circle will be unaffected. A live match may be suspended in the inner cone without ignition if not allowed to touch the sides of the flame-cone. The conical shape of the flame is due to the fact of the gas issuing from the jet in the form of a cylinder, and being under a little greater pressure than the air, assumes the form of a slightly diverging cone.

The gas first issuing from the jet burns as a ring around the orifice, the next layer of gas must pass above this ring in order to reach the air for its combustion. Each successive ring must pass through the preceding to reach the air and as each burning ring diminishes the volume of unburned gas these rings must grow smaller and the converging cone is the only possible form. This explanation holds for the shape of the candle flame or other flame resulting from the issuance of gas from a cylindrical wick.

Hydrocarbon Flames. It has already been stated that these bodies enter largely into the composition of all our common illuminating oils and gases. These bodies undergo decomposition during the combustion and the products of combustion are produced at successive stages. They give rise to flames more complex in structure than those just described. The common flames under this head are those of gas, oil, and the candle, the last will be described as typical of all.

In the first case the fuel is supplied at the burner in the gaseous state, the gas having been obtained from the destructive distillation of coal at a distance; in the second (oil) the fuel is liquid and is converted into gas at the lamp. In the candle the tallow or wax is solid, so that it must be melted and distilled during the operation of burning.

Candle Flame. In the candle flame there are three concentric cones; the interior is dark and is composed of unburned gas resulting from the destructive distillation of

the tallow, the next and the largest part of the flame, is brightly luminous and the outer cone is thin and only faintly luminous. There is also a bright blue cup at the base of the cone.

The flame-cone proper consists of the outside and faintly luminous cone, the next or luminous one, and the blue cup at the base; the interior dark cone consists of combustible gases to which air does not penetrate and is not part of the flame. In the luminous cone combustion is taking place, but the air supply is not sufficient for complete combustion. At the temperature of the cone there results a decomposition of some of the hydrocarbons with a separation of free carbon. This free carbon heated to whiteness by the burning hydrogen and other gases confers the great luminosity upon this cone. In the outer cone where the air supply is sufficient, more complete combustion takes place with production of great heat but little light.

The blue cup at the base is due to the perfect combustion of a thin layer of gas at that point and to the lower temperature due to the presence of an excess of air.

The combustible gases of the inner cone may be readily extracted and burned at some distance from the flame by inserting one end of an open glass tube six or more inches long into the cone.

The unburned carbon in the luminous cone can be shown by depressing upon it a white porcelain plate.

Flame for Special Purposes. *Lighting Flames.* From the foregoing considerations of the nature, properties, and structure of flames, it is evident that several considerations must enter into the construction of burners for different purposes. The Argand gas-burner is one of the most widely used burners for gas-lighting. The gas in this burner issues from the annular space between two concentric cylinders; the gas-flame is a hollow cylinder which is surrounded by the chimney and air is supplied to the flame both from the inside

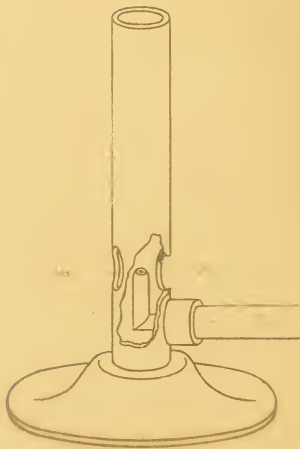




Fig 6
Candle Flame

and outside of the cylinder. The chimney acts effectively both in producing a draught and thus giving a liberal supply of air, which in combination with the regulated flow of gas permits the proper adjustment of the two for the best light. If there be too great a proportion of the gas some of the carbon escapes unburned and the flame smokes and the temperature is not high enough to produce a brilliant light. By using two chimneys and causing the air that feeds the flame to pass down between them, there is less chilling effect on the flame and an equal light may be obtained with a less consumption of gas. The Argand burner may be converted into the Welsbach, already referred to, by the insertion of a durable gauze cylinder into the flame and regulating the air and gas supplies so as to produce the highest temperature.

Smokeless Flames. Since luminous flames in general contain unburned carbon, they deposit soot when the flames come in contact with solids. When bodies are to be heated by flame as in laboratories and in kitchens, it is therefore advantageous to have flames in which the combustion is as perfect as possible, producing a smokeless flame.

Smokeless Flames. This result is accomplished by mixing the air and gas in certain proportions before combustion, so that the hydrocarbons are burned without the separation of carbon, this also causes the disappearance of the luminous part of the flame. By a proper adjustment of the air and gas the flame from the combustion of a given amount of gas is smaller and the temperature higher.

The principle upon which smokeless burners are constructed, is well shown in the Bunsen burner. This burner in its simplest form, consists of a cylindrical tube mounted on a substantial base. The gas is led in at the base and ascends the tube, near the bottom of which there are two holes for the admission of air. The flow of the gas draws air into the tube and the mixture is burned at the top of the tube. The holes for the admission of the air can be entirely

or partly closed. By entirely closing the air-holes the flame is white and luminous, by admitting the proper proportion of air the flame becomes smaller, of a blue color, and almost non-luminous. This loss of color was formerly supposed to be almost entirely due to the complete combustion of the hydrocarbons without the separation of the carbon. It is now known that the effect can be brought about by admixture with the hydrocarbons of other gases than air, as nitrogen and carbon dioxide. The loss of luminosity in the case of air is due partly to the more perfect combustion, to the cooling effect of the nitrogen, and to the fact that in the presence of nitrogen a higher temperature is required to decompose the hydrocarbons. The cooling effect of the nitrogen prevents the separation of the carbon at certain parts of the flame, but the more perfect combustion makes the temperature at other parts higher than the corresponding parts of the luminous flame.

The flame of the ordinary Bunsen burner consists of only two cones. The inner cone is a mixture of air and gas; combustion is taking place only in the outer one. That the flame does not travel inward is due to the rate of motion of the mixed gases; in the outer cone this speed is diminished so that the gases can be raised to the point of ignition. If the rate of flow of the gases be diminished the flame will penetrate further and further inward and can be made to strike down the tube to the point of inflow of the gas and air. The absence of flame in the inner cone of the Bunsen burner may be shown in the manner already given for common flames.

The Blow-pipe Flame. This flame is produced by forcing a stream of air across a common gas, candle, or lamp-flame. The mouth blow-pipe is an instrument of great utility. In its simplest form it consists of a bent tube terminating in a small end with an aperture. This flame shows three cones but they are peculiar in appearance being long and pointed.

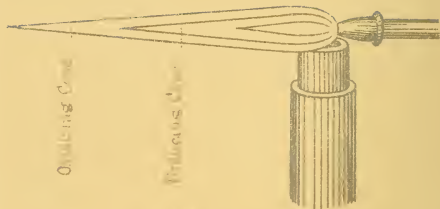


Fig. 6.
Flow of Flame

The innermost cone is composed of a mixture of air and combustible gases not in the state of combustion; the second cone is blue in color and consists of gases undergoing combustion but with an insufficient supply of air; the outer cone is but very faintly luminous and the combustion is there complete. The space between the outer and ~~middle~~ *inner* cone is filled with hot combustible matter which displays great reducing or deoxidizing power, especially is this so at the point of the second cone; this flame is accordingly called the *reducing flame*. Nearly any metallic oxide placed just in the tip of this cone is deprived of its oxygen and reduced to the metallic state.

The highly heated air just beyond the point of the outer cone oxidizes very readily, hence this outer cone is termed the *oxidizing flame*. In the mouth blow-pipe it must be understood that the air is not propelled from the lungs, but simply from the mouth by the muscles of the cheek. The current of air may be produced by a bellows or other mechanical means.

Oxyhydrogen Flame. By forcing a stream of pure oxygen through a gas flame, a blow-pipe flame of very high temperature may be produced. A flame from a mixture of hydrogen and oxygen in proper proportions gives the highest temperature obtainable by chemical means. In the production of the oxyhydrogen flame, the gases (hydrogen and oxygen) are usually led by tubes from separate holders to the jet or blow-pipe where they are burned and allowed to mix only just before burning. Special precautions are made in the blow-pipe so that the mixture can not there explode.

Safety Lamps. The temperature to which a gas must be raised in order that combustion may take place has already been defined as its ignition point, commonly called the kindling point. Combustion can not take place until this temperature is reached and if the temperature of the burning gas be reduced below this point the flame will be extinguished.

This fact may be simply illustrated with the candle flame by coiling a thin copper wire into a cylindrical spiral about one-half an inch long and of such diameter as to coincide with the flame-cone. If the coil be placed over the candle the flame will be extinguished, but if the coil be first heated and then placed over the flame it will shoot above the coil and continue to burn.

A copper wire-gauze of sufficiently fine meshes may be placed over a gas jet and the flame will not extend above the gauze, or if the gas be lighted above the gauze the flame will not pass below. In each of these cases the temperature of the burning gases is reduced below the kindling point and combustion ceases.

Different substances have different ignition points and owing to this fact a wire-gauze through which a marsh gas flame will not pass readily, permits the passage of the hydrogen flame.

The above considerations make clear the principles of safety lamps. The most celebrated of these is Davy's miners' lamp. This is an oil lamp the flame of which is enclosed in a cage of wire gauze made double at the upper part where the heat of the flame is most felt. The gauze has 400 or 500 meshes to the square inch. The lamp is so arranged that the reservoir can be supplied with oil and the wick trimmed without unscrewing the cage and thereby exposing the flame of the lamp.

In an explosive atmosphere of marsh gas and air, the fire-damp may burn within the cage but the flame will be extinguished by the gauze and not ignite the mixture outside.

The lamp thus serves to give indications of the state of the atmosphere in a mine and enables an examination to be made without risk to the inspector. This is the true use of the lamp and it is not intended to enable workmen to labor in an explosive atmosphere.

Stephenson's Lamp. Stephenson's original safety lamp was constructed upon the principle that the explosive mixture could be carried by the flame so rapidly that there would not be time for the mixture to be raised to the igniting point. This rapid flow of the gases was accomplished by a tall chimney producing a powerful draught. If the velocity of the gases be greater than the rate of propagation of combustion in the mixture the flame will not spread. This principle has already been referred to in explaining the hollow structure of the Bunsen flame.

The explosions which have so often proved disastrously fatal in coal mines and which the safety lamp is intended to help prevent, have in most cases been due to explosive mixtures of marsh gas, other hydrocarbons, and hydrogen with the air. Fine coal dust in the air of the mine increases the liability to explosion and in some cases this dust has been the sole cause of explosion.

Explosions have occurred in flour mills through the general diffusion of flour dust throughout the building. Any readily combustible substance thickly distributed as fine dust through the air will burn with explosive effect.

Slow and Flameless Combustion. There are several substances which possess the power of causing the slow combustion of certain gases. Finely divided platinum or even platinum foil will bring about the combination of hydrogen and oxygen. A clean thin strip of platinum foil put into a jar containing a mixture of hydrogen and oxygen, will immediately cause their combination to begin, and if the foil be very thin its temperature may rise to redness and cause the explosion of the remaining mixture.

If the platinum be reduced to the state of minute division as is the case of platinum black or its surface greatly extended as in spongy platinum, it immediately becomes red hot in a mixture of hydrogen and oxygen. Hydrogen falling upon platinum black in air is immediately ignited. Upon

this principle lamps for ~~instantaneous~~^{automatic} light have been constructed.

If a thin piece of platinum foil be heated but not sufficiently to emit light, and held in a jet of gas escaping from a Bunsen burner, its temperature will rise to redness and it will continue to glow as long as the mixed gases impinge upon it. This is a case of flameless combustion. The same result may be brought about in vapor of alcohol and ether.

Although platinum possesses this property to a marked degree, it is not limited to this metal; palladium and gold display it to a less degree while glass and certain stones show it to a still lower degree.

A full explanation can not be given of these results, but they are due to the property which the solids possess of condensing gases upon their surfaces or of absorbing them and bringing them under the temporarily changed conditions within their sphere of mutual action.

When the ignition point of a substance is lower than the temperature produced by its combustion, it will burn when once ignited; but when the reverse is the case there will be required a continual application of external heat to keep up the combustion.

SILICON.

In many of its chemical relations silicon resembles carbon, but while the latter is the characteristic element of the organic kingdom the former is one of the most abundant elements of the mineral world.

Silicon is not known to occur in the uncombined state, but in combination it is next to oxygen the most abundant and widely distributed element. In combination with oxygen, as silicon dioxide (silica), it occurs in sand and the various forms of quartz, which are among the most common and abundant forms of natural minerals. It also exists very widely in the silicates which result from the combination of silica with various metallic oxides. These silicates form the

great mass of the rocks which make up the earth's crust. Silicon oxide is also found in certain species of the vegetable kingdom.

The element silicon is of no practical importance; it has been obtained both in the amorphous and crystalline forms, being in the first a dark brown powder and in the second of a metallic lustre resembling graphite. The powder burns vividly in oxygen until covered by a coating of silica; the graphitic form is incombustible. The amorphous form readily attacks platinum when heated with it. It is claimed by some that there is a third form of silicon corresponding to the diamond form of carbon.

Preparation of Silicon. Silicon may be prepared by decomposing potassium silico-fluoride at high temperature by potassium as indicated by the reaction, $\text{K}_2\text{SiF}_6 + \text{K}_4 = \text{Si} + 6\text{KF}$. After cooling the potassium fluoride is dissolved out by water.

SILICA; SiO_2 .

The only oxide of silicon, silica (SiO_2), is a very important compound. Alone or in combination it forms a very large proportion of the earth's crust. The purest natural form of silica is rock crystal, a clear transparent variety of quartz. The dense white varieties of sand are nearly pure silica; in a less pure form silica and the silicates constitute the greater part of nearly all soils. Its action in soils seems to be mainly mechanical as silica takes but little part in the direct sustenance of plants. It serves as a receptacle or basis through which the other ingredients of the soil are distributed. Its chemical and physical stability admirably fit it for this purpose. Silica is found in the outer sheaths of certain grasses and reeds and as tabasheer in the joints of the bamboo. This fact proves its solubility to a certain extent otherwise it could not be taken up by plants. Many hot springs and geysers also dissolve it. It is deposited in large quantities by the springs and geysers of the Yellowstone Park.

The natural varieties of silica are insoluble in pure water but hot alkaline solutions readily dissolve the amorphous

varieties and under high temperature and pressure also dissolve many of the crystallized forms.

Silica is essentially an acid oxide forming salts with many metallic oxides. Owing to its non-volatility, it decomposes all salts of volatile acids when highly heated with them. It thus replaces acids which at a lower temperature displace it. When heated with bases, silica generally unites with them forming silicates. The silicates are the most common and abundant of minerals. As feldspars and micas the silicates enter largely into the composition of granitic rocks and the different varieties of clay are hydrous silicates of aluminum. Common glass is a mixture of several silicates. The silicates as a class are all insoluble except certain alkaline silicates in which there is a large proportion of the base.

Silicic acid is generally represented as tetra-basic and the formula written H_4SiO_4 , or SiO_2 with $2\text{H}_2\text{O}$, but the formulæ of many of the silicates indicate their derivation from silica combined with more or less than two molecules of water.

A compound consisting of silicon and carbon (SiC) can be prepared by heating silica with carbon in an electric furnace. The compound is called *carborundum* and has come into considerable prominence lately as an abrasive. It is made in large quantity at Niagara Falls.

BORON.

This element has not been found in the free state. In combination it is almost entirely confined to the mineral kingdom though its presence has been detected in grape vines and a few other plants. It is the basis of boric acid in which combination it is found in certain volcanic waters and forming many borates of the metals, one of the most important and common of which is sodium borate or tincal.

The element may be obtained by heating boron trioxide with potassium. $\text{B}_2\text{O}_3 + 3\text{K}_2 = \text{B}_2 + 3\text{K}_2\text{O}$. In this manner boron is obtained as a dark brown powder.

Boric Oxide and Acid. Boron forms but one oxide the formula of which is B_2O_3 . This oxide forms three oxy-acids. The native acid found in volcanic regions is tribasic represented by the formula $3\text{H}_2\text{O}$, B_2O_3 or H_3BO_3 , but is converted into other forms by the action of heat; at red heat all the water is driven off.

The acid is an antiseptic and is sometimes used alone or with glycerine to preserve meats and other food. The solution of the acid in alcohol imparts a green color to the flame of the vapor. It will give color to steam issuing from a boiling solution of the acid if a flame be held in the steam.

Borates. At high temperature boric oxide combines with many metallic oxides giving glassy borates which often have characteristic colors—upon this property depends the main use of boric acid in the arts. The formulæ of most of the borates do not indicate their derivation from a tribasic acid. Borax or sodium borate is one of the most important of this class of salts. Borax occurs native in tinal. It is readily prepared by the action of boric acid on sodium carbonate. It will be further mentioned under sodium.

COMPOUNDS OF HYDROGEN AND NITROGEN.

Ammonia (NH_3). This is a compound of hydrogen and nitrogen indicated by the formula NH_3 . It is primarily of organic origin and results from the putrefaction of organic matter, from the destructive distillation of coal, bones, and other organic matter. It is constantly removed from the air through absorption by rain and by the soil. It has been found in the emanations of volcanoes. In the combined form it is frequently present in beds of guano (the excrement of sea fowls) and as the chloride and sulphate in certain volcanic regions. It is also present in small quantity as carbonate, nitrites, and nitrates in soils and water where, in the last named forms, it becomes available for plant food.

Animals during life, and both plants and animals after death return to the air in the form of ammonia the nitrogen which existed in their organisms and possibly some of it is returned as free nitrogen. They thus return to the air the ammonia which was taken from it. The manner in which the nitrogen of the air was originally made available for food and started upon its endless circuit has been difficult to determine and even now is not thoroughly understood. It has lately been found that certain species of bacteria exist which are capable of oxidizing the nitrogen of the air and thus starting it upon the cycle of plant service. One form of these

bacteria is found to ply its vocation in connection with the growth of leguminous plants having their homes in the roots of the plants. It is also found that bacteria are instrumental in transforming the nitrogen of dead organic matter into available shape for plant use again.

Physical Properties of Ammonia. Ammonia is a colorless gas, having a strong, pungent odor which excites to tears. It has a caustic, burning taste. Its specific gravity is eight and one half referred to hydrogen. It is liquefied by a temperature of -40° C. at atmospheric pressure, or by a pressure of six and one half atmospheres at 10° C. In the liquid state it is a colorless mobile liquid which at 0° C. has a specific gravity .62. Its boiling point is -33.7° C. under atmospheric pressure.

During the evaporation of liquid ammonia great reduction of temperature takes place and it has for this reason been frequently used in the artificial production of cold for freezing, or other purposes.

Gaseous ammonia is more readily soluble than any other gas, water at 15° C. dissolving over 750 times its volume, the volume of the solution being something more than one and one half times that of the water.

During the solution of the gas more heat is evolved than corresponds to the liquefaction of the gas, which can only be attributed to chemical action. The gas however can be entirely removed from the water and no definite compound of the two is known. The solubility of the gas increases as the temperature of the water diminishes. The great solubility of ammonia in water may be strikingly illustrated by filling a bottle with ammonia by displacement over mercury, making the mouth of the bottle air-tight and transferring to a vessel of water; when the stopper is removed the water immediately fills the bottle and if the water be admitted by a tube through the cork it will play as a fountain.

In Carré's freezing apparatus for ice, liquid ammonia is

allowed to evaporate from a strong iron receiver which surrounds the water to be frozen. The vapor of the ammonia is absorbed by water contained in another receptacle, so as to increase the rapidity of evaporation from the receiver. The ammonia can then be driven out of the water in the second vessel by heat and condensed by its own pressure in the receiver and the operation repeated. The boiler is of course allowed to cool before evaporation from the receiver begins.

Chemical Properties of Ammonia. Ammonia is alkaline to a very high degree; it has the alkaline action on vegetable coloring matter and combines with acids, neutralizing them completely. It can be kindled in the air, but will not continue to burn when the external source of heat is removed. In an atmosphere of pure oxygen the ammonia burns with a continuous flame.

It is decomposed into its elements by passage through a red hot tube, two volumes of ammonia producing one volume of nitrogen and three volumes of hydrogen. Ammonia escaping into an atmosphere of chlorine takes fire and burns producing ammonium chloride.

Its solution is largely used in the arts and as a reagent in the chemical laboratory. By neutralizing the solution of ammonia with the mineral acids, salts are obtained bearing strong resemblance to the corresponding salts of sodium and potassium. This taken in connection with the other strong alkaline characters, has given rise to the suggestion that the solution of ammonia contains an alkaline hydroxide (NH_4OH) similar to KOH and NaOH , in which NH_4 performs the same function as potassium and sodium.

This hypothetical radical (NH_4) is called ammonium. The salts from the solution of ammonia may be considered as formed either by the direct union of ammonia with the acids or by the replacement of the hydrogen of the acid by ammonium; in the latter case ammonium acts similarly to

the metals in forming salts. The salts of ammonium will be more fully described in connection with the metallic salts. Ammonia is easily expelled from its salts by heating with slaked lime or a solution of potash or soda. On account of its striking odor this gives a ready test for such a salt.

Preparation of Ammonia. There are many sources from which ammonia may be obtained, but the chief source is the ammoniacal liquor of the gas-works. The manufacture of gas will be described later, at present it is sufficient to know that ammoniacal liquor results from the destructive distillation of coal in the manufacture of gas. This liquor contains several compounds of ammonia, two of the most important of which are the carbonate and hydrosulphide $(\text{NH}_4)_2\text{CO}_3$, and NH_4HS . The liquor containing these substances is heated with lime in a still, the lime displaces the ammonia from combination and it is conducted into a tank containing sulphuric or hydrochloric acid. The acid combines with the ammonia forming ammonium sulphate or chloride, depending upon the acid used. There is always some hydrogen sulphide driven off in the operation, but this escapes from the receiving tank and is burned.

The sulphate of ammonia is the form in which the ammonia is generally sold for fertilizing. The chloride after purification by heating and sublimation is used for various purposes and is the form generally used to give pure ammonia. From the chloride, ammonia is readily obtained by heating it with powdered lime as indicated by the reaction, $2\text{NH}_4\text{Cl} + \text{CaO} = \text{CaCl}_2 + \text{H}_2\text{O} + 2\text{NH}_3$.

The gas may be conducted into a vessel of water until a solution of the required strength is obtained. By this means liquor ammonia is prepared as an article of commerce.

The most convenient way of obtaining ammonia for laboratory purposes is to gently heat liquor ammonia; the gas passes from the solution very readily and may be collected

by downward displacement or over mercury. The gas may be readily prepared for laboratory use directly from the chloride as above indicated if the liquor ammonia be not on hand.

In the above method of separating the ammonia from the ammoniacal liquor of the gas-works, the ammonia was displaced from its combination by another base, lime being used. It is possible (and sometimes done) to treat the ammoniacal liquor with an acid (sulphuric or hydrochloric) which combines with the ammonia and liberates carbon dioxide and hydrogen sulphide. But the sulphate or chloride thus produced is mixed with many other constituents of the liquid and is more difficult to purify.

Other sources for the commercial preparation of ammonia are the blast furnaces and coke ovens; the ammonia in these cases also resulting from the destructive distillation of coal.

Although the direct combination of nitrogen and hydrogen is only accomplished with difficulty, this compound is sometimes produced when nitrogen is brought into contact with nascent hydrogen.

Hydrozine or Hydrozoic Acid. There are two other compounds of nitrogen and hydrogen hydrozine (N_2H_4) and hydrozoic acid (N_3H), but they have up to the present time received no useful application.

COMPOUNDS OF NITROGEN AND OXYGEN.

These elements under ordinary conditions show no disposition to enter into combination, however there are five distinct compounds of them known; viz., N_2O , NO , N_2O_3 , $NO_2=N_2O_4$, and N_2O_5 . These formulæ show that the quantities of oxygen that unite with a given quantity of nitrogen are to each other as 1 : 2 : 3 : 4 : 5.

There are three oxy-acids of nitrogen corresponding to the first, third and fifth of these oxides.

The compositions of these acids and their relations to the corresponding oxides will be seen from the following formulæ:

$\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$	Hyponitrous anhydride.	$\begin{smallmatrix} \text{N} \\ \text{H} \end{smallmatrix}$	Hyponitrous acid.
$\begin{smallmatrix} \text{NO} \\ \text{NO} \end{smallmatrix} \text{O}$	Nitrous anhydride.	$\begin{smallmatrix} \text{NO} \\ \text{H} \end{smallmatrix} \text{O}$	Nitrous acid.
$\begin{smallmatrix} \text{NO}_2\text{O} \\ \text{NO}_2 \end{smallmatrix}$	Nitric anhydride.	$\begin{smallmatrix} \text{NO}_2\text{O} \\ \text{H} \end{smallmatrix}$	Nitric acid.

The first two acids have not been obtained in a free or pure state and are known from their salts.

The third is the most important of these acids and is the one from which all the compounds of nitrogen and oxygen are obtained directly or indirectly.

NITRIC ACID.

Preparation. The combination of oxygen and nitrogen can be brought about directly by artificial means, and in the presence of water nitric acid results but the acid is always prepared from natural nitrates.

The manufacture of nitric acid is a commercial process and is accomplished by heating sodium nitrate with sulphuric acid in suitable retorts, usually in cast iron cylinders.

The proportion of the reagents and the final reaction are indicated by the equation, $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HNO}_3$. The nitric acid vapor produced is conducted from the retorts into stoneware or other suitable receivers in which it is condensed, the receivers being cooled by water. During the operation some of the vapor of the nitric acid is decomposed thus, $2\text{HNO}_3 = \text{H}_2\text{O} + \text{O} + 2\text{NO}_2$, the last product being a red vapor which in the solution of the condensed acid gives it a yellowish-red color.

Pure nitric acid is colorless, but if exposed to sun-light the above reaction takes place with the resulting color. The oxygen thus liberated exerts a pressure on the acid in the bottle and may result in ejecting some of the liquid when the stopper is withdrawn. The strongest acid in the commercial manufacture is obtained by using pure reagents and collecting the middle portion of the distillate separately. For the most concentrated colorless acid some other precau-

tions are necessary. The strength of the acid is indicated by the specific gravity; the strongest has the specific gravity 1.53, common aquafortis has the specific gravity of 1.30 and contains less than 50 per cent of acid.

On a small scale in the laboratory the acid may be made from either potassium nitrate or sodium nitrate by heating the salt with sulphuric acid in a glass retort and condensing the acid in a flask cooled by a wet cloth. In the laboratory method it is better to use the reagents in the proportions indicated by the following reaction, $\text{KNO}_3 + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HNO}_3$, for this reaction requires lower temperature and the acid salt is more easily dissolved out of the retort than would be the normal sulphate, which would be formed were double the amount of nitrate used. A given quantity of Chili saltpetre will produce more acid than the same weight of common nitre.

In India and other dry countries potassium nitrate occurs in certain places as an efflorescence on the surface of the soil. This is the principal source of nitre. Sodium nitrate or Chilian saltpetre occurs as immense beds along the northern coast of Bolivia and Peru.

Properties of Nitric Acid. Nitric acid when pure is a colorless liquid which fumes strongly in the air owing to condensation of the acid vapor by the aqueous vapor of the air. It has a very choking, suffocating smell. It is very corrosive, the strongest acid produces painful sores when brought into contact with the skin, and the dilute acid turns the skin and other organic matter yellow. A drop of sulphuric or hydrochloric acid will stain cloth red and the color may be partially or wholly restored by prompt application of ammonia while the stain of nitric acid is intensified by ammonia though the corrosive action is prevented.

Under ordinary conditions strong nitric acid is weakened and weak nitric acid strengthened by boiling, until an acid of 68 per cent is reached when the whole distils over without

any change. If the pressure under which the distillation occurs be varied the strength of the distillate will also vary.

Nitric acid is a powerful oxidizing agent, very few substances being able to withstand its action. Phosphorus dropped into a dish containing strong nitric acid is oxidized, often with such energy as to give flame, P_2O_5 being produced.

Sulphur is oxidized by hot nitric acid to sulphur trioxide SO_3 . Finely divided carbon or sawdust may be set on fire by strong nitric acid.

Nitric acid acts upon some organic substances so readily as to inflame them. A small quantity of oil of turpentine poured upon strong nitric acid in an open capsule ignites with some violence. Hair or silk may be made to take fire by holding it in the vapor of boiling nitric acid.

Nitric acid acts upon all the common metals except gold, platinum and aluminum. It generally forms nitrates but sometimes only oxidizes the metals. Owing to its strong oxidizing power hydrogen is never evolved by the action of this acid upon the metals. The hydrogen displaced by the metal is oxidized by the remaining acid present. It has been shown that if nitric acid is entirely free from nitrous acid it acts very slowly if at all upon many metals.

In addition to the actions above named, nitric acid acts upon a variety of organic compounds, one or more atoms of the hydrogen of the organic compound being replaced by one or more molecules of NO_2 . The resulting compounds are nitro-substitution compounds and will be referred to again.

Nitric acid is mono-basic.

Uses. Nitric acid is of great importance in the arts; among its most important uses may be mentioned the manufacture of coal-tar colors, the preparation of nitro-compounds which include nearly all the high explosives, of many nitrates used in the arts, and the refining of gold and silver. An alloy of copper with gold is readily detected by

touching it with nitric acid when the copper present will give the green nitrate.

It is remarkable that the dilute acid generally acts more readily than the concentrated.

Nitrates. The nitrates constitute a very important class of salts. They are all decomposed by heat and are soluble in water (with unimportant exceptions). They are, like the acid, oxidizing agents. Powdered lead nitrate and charcoal may be exploded by a blow. Common nitre is used in gunpowder because of its oxidizing power and several other nitrates are employed in other explosives.

The negative chemical properties of nitrogen, its little disposition to combine with other elements and its character as a permanent gas are probably at the basis of the instability of its compounds, to which we shall have frequent occasion to refer.

The nitrates being generally soluble the acid can not be precipitated and it is not so easily detected in solution as the other common mineral acids. The easiest test is as follows—add to the suspected solution in a test tube, a solution of iron sulphate; then introduce below the mixed liquids concentrated sulphuric acid if there be present any nitrate, the sulphuric acid will liberate the nitric acid and the ferrous sulphate reduces it to NO_2 which colors the two liquids at the surface of their junction.

Nitrous Oxide, Laughing Gas, N_2O . This gas may be obtained by heating ammonium nitrate in a Florence flask fitted with cork and delivery tube. It may be collected by displacement over warm water or mercury. The nitrate should be heated gently or nitric oxide will be produced.

Properties. N_2O is a colorless transparent gas with a slight odor and sweetish taste. It is more soluble than oxygen, water dissolving its own volume at 10°C . It supports ordinary combustion like oxygen; the combustion is due to the oxygen, the nitrogen monoxide being decomposed and the nitrogen set free. Carbon burned to carbon dioxide in nitrogen monoxide produces more heat than when burned

in oxygen which shows that heat is evolved in the decomposition of nitrous oxide and must have been consumed in its production. A substance which absorbs heat in its production is called *endothermic*, one which gives it out *exothermic*.

Laughing gas is used as an anæsthetic in dental surgery. It may be drawn into a test tube in the liquid state from the holder. The liquid supports combustion. It may be distinguished from oxygen by its greater solubility and sweetish taste.

Nitric Oxide, NO. This oxide is readily obtained by the action of dilute nitric acid upon copper. The metal is oxidized and the acid deoxidized with the separation of nitric oxide, the oxide formed is acted upon by another portion of the acid and copper nitrate is formed. The nitric oxide is a colorless transparent gas, but in contact with oxygen it unites with it, giving the nitrous oxide if the oxygen be in excess, otherwise some trioxide is formed, giving a very characteristic reddish brown vapor. The presence of oxygen may be readily detected by the addition of this gas. It will support combustion if the temperature of the burning body is high enough to decompose the gas.

OTHER OXIDES OF NITROGEN.

Nitrous Anhydride, N_2O_3 . There is still some uncertainty as to the existence of this compound. The substance generally assumed to be N_2O_3 is very probably a mixture of nitrous and nitric oxides. A solution of the substance is believed to contain nitrous acid, though the acid has not been isolated.

Nitrogen Tetroxide. This substance is the main result of the action of oxygen upon the nitric oxide. This gas possesses the property of combining directly with certain metals forming nitro-metals. The tetroxide will support combustion if the temperature of the burning body be high enough to decompose the gas.

Nitrogen Pentoxide, N_2O_5 . The pentoxide may be obtained by dehydrating nitric acid with phosphorus. It is a white crystalline substance. It is very unstable and when suddenly heated explodes with violence. It dissolves in water forming nitric acid.

CHLORINE; Cl.

Chlorine has not been found in the uncombined state in nature. It is a member of an important natural group including iodine, bromine, and fluorine. On account of the

occurrence of the first three in the salts of sea water, the group has been called the *halogens*, and their compounds the *haloid compounds*.

In combination with the metals, chlorine is of abundant occurrence, the most common chloride being sodium chloride, common salt. In the Stassfurth deposits potassium chloride is also an abundant constituent. Many other chlorides occur native.

The chlorides of sodium and potassium, especially the latter, are found in animal secretions. Chlorine is also found in combination with hydrogen as hydrochloric acid, in the gases issuing from certain volcanoes.

Preparation of Chlorine. Chlorine may be extracted from common salt by heating a mixture of the salt and manganese dioxide with dilute sulphuric acid. The reaction is indicated by the equation $2\text{NaCl} + \text{MnO}_2 + 2\text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$. Chlorine may also be obtained from hydrochloric acid by gently heating manganese dioxide with it, as indicated by the equation, $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$. This gas is a very offensive one to deal with and special precautions and care should be taken in obtaining and manipulating it. On the manufacturing scale chlorine is obtained by the second method.

Chlorine is now prepared on the manufacturing scale in Europe by the electrolysis of common salt. The same process is employed in this country to prepare sodium hydroxide but the chlorine, so far as can be learned, is wasted.

Physical and Chemical Properties. Chlorine is a greenish yellow gas, with a specific gravity of 35.5 referred to hydrogen. It has a disagreeable suffocating odor and is easily liquefied. At ordinary temperature water dissolves about two volumes of the gas. For experimentation chlorine is collected by displacement, or over tepid water; it acts upon mercury and there is considerable loss in collecting it over

cold water. A strong brine solution dissolves it much less readily than water.

Chlorine has powerful affinities and unites with a great number of the other elements even at ordinary temperature. Its affinities do not extend to oxygen but are strongly exerted towards hydrogen and the metals. Its affinity for hydrogen is its most distinguishing characteristic.

It combines directly with hydrogen, bromine, iodine, sulphur, arsenic and phosphorus. Phosphorus finely divided or a well dried piece, will take fire in chlorine; powdered arsenic dropped into the gas inflames.

It combines directly and at ordinary temperature with nearly all the metals. Powdered antimony and several other metals in the form of thin leaf take fire when dropped into the gas.

On account of its affinity for hydrogen a lighted wax taper plunged into the gas will continue to burn with a smoky flame, the hydrogen of the taper burning, the carbon being separated.

For the same reason many of the hydrocarbons will take fire spontaneously; a strip of bibulous paper wetted with oil of turpentine and plunged into the gas bursts into flame with a copious liberation of soot—a mixture of chlorine and acetylene explodes violently when exposed to light.

Chlorine is not capable of direct combination with carbon, which fact accounts for the separation of the carbon in the cases just cited.

On account of its attraction for hydrogen it will decompose water if the solution be exposed to light. A mixture of hydrogen and chlorine can be kept in the dark, but if exposed to diffused daylight they combine quietly, if to direct sunlight, they combine suddenly with explosion.

Uses. The most useful applications of chlorine depend upon its affinity for hydrogen. Its most valuable property from an industrial point of view is its bleaching power.

Chlorine poured into a solution of indigo or other vegetable coloring matter will rapidly discharge the color. The same action is observed if cloth dyed with vegetable colors be dipped in a solution of chlorine. Colored flowers are bleached when dipped into a jar of the gas.

For bleaching it is essential that water be present, as perfectly dry chlorine does not even affect litmus. The chemistry of the process seems to be due to the action of the chlorine upon the water, liberating the oxygen, which in connection with the chlorine converts the coloring matter into oxidized or chlorinized products, which are colorless or nearly so.

Chlorine is largely used in the arts for bleaching linen and cotton goods and rags for the manufacture of paper. Silken and woolen goods would be injured by chlorine and are bleached with sulphurous acid gas. For bleaching purposes neither the gas nor its solution is so convenient as the combined form, hence it is generally employed in the form of bleaching powder called chloride of lime, from which the gas is easily liberated as desired.

Chlorine is also one of the best deodorizers; by virtue of its affinity for hydrogen it breaks up and removes from the air hydrogen sulphide and ammonia both of which result from the putrefaction of organic matter and are very objectionable. Chlorine is also used as a disinfectant; its affinity for hydrogen and its oxidizing power enable it to destroy certain micro-organisms which are injurious to health.

Liquid chlorine is now an article of commerce; it is put up and transported in iron bottles lined with lead; it is used in the extraction of gold from its ores.

HYDROCHLORIC ACID; HCl.

Occurrence. It occurs in nature in the gases emitted from volcanoes and has also been found in the spring waters of volcanic districts.

Preparation. Hydrochloric acid may be produced by the direct union of the elements but for use it is always prepared by acting upon sodium chloride with sulphuric acid as indicated by the following reaction, $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$; the gas may be collected by displacement or over mercury. By using the proper proportion of the ingredients and a higher temperature the reaction for the production of the acid can be made to take the form, $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$.

Hydrochloric acid was formerly obtained in enormous quantities as a bye-product in the Leblanc process of manufacturing sodium carbonate, the first step in the operation being indicated by the above reaction. The manufacturer of the alkali was compelled to prevent the escape of the liberated acid into the air because of its destructive action upon vegetation. Owing to changes in the methods of making alkali the hydrochloric acid is now a principal product in the Leblanc method.

The acid vapors resulting from the action of the sulphuric acid upon the salt, are thoroughly cooled and then brought into contact with a large surface of water by which the acid is absorbed.

Properties. Hydrochloric acid is a colorless gas with choking pungent odor. It fumes strongly in the air by condensing the moisture there present. Its formula shows it to be heavier than air. It is very soluble in water, one volume of water at ordinary pressure and 0°C . dissolves 500 volumes of the gas. As is generally the case the solubility decreases as the temperature rises. The solubility of the gas may be illustrated in the same manner as with ammonia.

The common liquid designated as hydrochloric acid is a solution of the gas in water, the strongest solution at 8°C . and ordinary pressure contains 43.8 per cent of the acid and has a specific gravity of 1.22. The strength of the acid may be inferred from its specific gravity.

If a weak solution of the acid be boiled, it loses water and becomes stronger; if a strong solution be boiled it loses acid and becomes weaker until in each case the solution contains 30 per cent of the acid when this solution distils over at a temperature of 110°C . This would seem to indicate a definite compound between the water and acid in the proportion named, but this proportion changes with the pressure.

Commercial hydrochloric acid is usually yellow from impurities. It is very likely to contain some chlorine, some sulphuric acid, some arsenic, and some iron chloride. Mixtures of snow or powdered ice and hydrochloric acid make very convenient refrigerants.

Hydrochloric acid is readily liquefied by cold and pressure. The liquid acid is colorless, with a specific gravity of .9. The liquid acid is almost without action upon most of the metals which are readily attacked by the aqueous solution. The liquid acid does not act upon lime. Dry hydrochloric acid gas does not act upon calcium carbonate.

Action of Hydrochloric Acid upon the Metals and Metallic Oxides. All the metals which decompose water will more readily act upon hydrochloric acid liberating hydrogen and forming a chloride. Sodium, potassium, zinc, iron, and tin are examples. Hydrochloric acid does not readily act upon aluminum and when boiling to a slight extent upon silver.

The acid acts upon metallic oxides, forming a chloride and water, two atoms of chlorine replacing one atom of oxygen. Those oxides to which there are no corresponding chlorides (the less basic oxides) frequently evolve chlorine from the acid. Thus while the lower oxide of manganese forms manganese chloride (MnCl_2), MnO_2 evolves chlorine; $\text{MnO} + 2\text{HCl} = \text{MnCl}_2 + \text{H}_2\text{O}$; $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$. Of the common metals the dichlorides are soluble in water except the dichloride of lead, the monochlorides are soluble except those of silver and mercury. Any soluble chloride in solution gives upon the addition of silver nitrate a white

curdy precipitate of silver chloride, which blackens upon exposure to light and is readily soluble in ammonia. This is a very characteristic test for a chloride in solution.

AQUA REGIA; NITRO-MURIATIC ACID.

This is a name given to a mixture of three volumes of hydrochloric acid and one of nitric acid. The mixture will dissolve gold or platinum while neither of the acids singly will do it. A chloride of the metal is formed and the power of the mixture depends upon the chlorine liberated. $\text{HNO}_3 + 3\text{HCl} = 2\text{H}_2\text{O} + \text{NOCl} + \text{Cl}_2$.

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine and oxygen have not been made to combine directly but there are known two oxides of chlorine and four oxy-acids; the oxides are ClO_2 and Cl_2O . The oxides are very unstable bodies and dangerous to handle because of their explosive character.

The oxy-acids of chlorine are *hypochlorous* (HClO), *chlorous* (HClO_2), *chloric* (HClO_3), and perchloric (HClO_4). The salts of the first and third are of considerable importance. Some of the metallic hypochlorites are useful in bleaching and potassium chlorate is of practical importance as an oxidizing agent; these salts will be referred to under the metals from which they are formed.

COMPOUNDS OF CHLORINE WITH CARBON, SILICON, BORON, AND NITROGEN.

Although chlorine does not combine directly with carbon, several chlorides of carbon can be obtained by indirect means as by the action of chlorine upon the hydrocarbons one atom of chlorine removing and combining with one atom of hydrogen and another atom of chlorine taking the place of the removed atom of hydrogen. This mode of substitution is called metalepsis. Chlorine combines directly with silicon and boron. With nitrogen it forms a very explosive compound indicated by the formula NCl_3 . This compound is formed by the action of chlorine upon ammonium chloride and is very dangerous to handle.

BROMINE; Br.

Occurrence. Bromine is not found free in nature. It occurs mainly in combination with potassium, sodium, and magnesium in small quantities in sea water; more abundantly in certain mineral waters as at Kissingen and in the

mother liquor of the salt works at Stassfurth, Germany, and of several of the salt works of the United States. Most of the bromine consumed in the United States comes from the mother liquor of the salt works in the United States and some from Stassfurth. It is obtained in greater quantity from the Ohio brine wells, and some from those of Pennsylvania, West Virginia and Michigan.

Preparation. After the less soluble salts are separated from the mother liquor by evaporation and crystallization, the liquor is introduced into a still and acted upon by chlorine. The chlorine liberates the bromine which is distilled off by passing steam into the still. The chlorine may be produced in the same still or introduced from a separate retort.

Properties. Bromine is the only non-metallic element which is liquid under ordinary conditions; it has a distinct red color; at 15° C. it has a specific gravity of 3. It emits an orange reddish acrid vapor which is very irritating and disagreeable, more so than that of chlorine. Three parts dissolve in 100 parts of water by weight. In its chemical attributes it resembles chlorine; it combines directly with many metals and non-metals and bleaches like chlorine.

Little use has been made of bromine since chlorine can generally be used for the same purposes and is much more abundant. It has, however, been used as a disinfectant, in the manufacture of coal tar dyes, and in analytical chemistry; for the last it is much more convenient than chlorine, being a liquid. For disinfecting the liquid is absorbed by cakes or sticks of kieselguhr or other porous earth made plastic by molasses. These sticks absorb a large amount of bromine and are kept in tightly stopped bottles.

Several bromides are employed in medicine and in photography. Bromine is soluble in carbon disulphide and ether.

Hydrobromic Acid; HBr. Bromine combines directly with hydrogen forming hydrobromic acid (HBr), corresponding to hydrochloric acid (HCl).

Oxy-Acids of Bromine. No oxides of bromine have been obtained but there are two oxy-acids similar to the corresponding chlorine acids. Hypobromous acid (HOBr) and bromic acid (HBrO₃).

IODINE; I.

Iodine has not been found in a free state; in nature it occurs in combination, principally with potassium, sodium, magnesium, and calcium as iodides or together with these metals and oxygen as iodates. Iodine is found in sea water, in many mineral waters, and as sodium iodate (NaIO_3) in the Chilian nitre beds.

Preparation. The two principal sources of iodine are kelp (the ashes of sea weed) and the native Chilian saltpetre or "Caliche," the latter source now furnishes the greater proportion of iodine.

Many varieties of sea-weed extract the iodine from sea water as a necessary portion of their food; when these weeds are burned the iodine is left in the ashes or "kelp," together with a large number of other salts. The iodine is mainly in the form of iodides of sodium and potassium. These iodides are separated from the other salts as perfectly as possible and then the iodine is liberated by the combined action of sulphuric acid and manganese dioxide exactly as chlorine is liberated from common salt.

In the "Caliche" the iodine is in the form of sodium iodate (NaIO_3) from which it is precipitated by the action of acid sodium sulphite.

Properties. Iodine is a crystalline solid of a bluish black color resembling graphite. In the solid state its specific gravity is nearly 5. It volatilizes sensibly at ordinary temperature diffusing an odor resembling that of chlorine. It fuses at 114°C. and gives a beautiful violet vapor which is one of the heaviest known gases being nearly nine times as heavy as air. At a higher temperature the color of the vapor changes and its density becomes less.

It is slightly soluble in water, readily soluble in carbon disulphide, benzene, petroleum spirit, and solution of potassium iodide and alcohol.

In chemical properties it resembles chlorine and bromine but is less energetic being displaced from its compounds by these elements. It combines directly with many elements both metallic and non-metallic. Phosphorus placed in contact with powdered iodine at once takes fire, as also does

powdered antimony when dropped into iodine vapor. In the presence of water it attacks gold. When brought into contact with starch it gives a sky blue color; this is a very delicate test for free iodine and will reveal the presence of a millionth part in any liquid; iodine in combination will not affect the starch.

Uses. Iodine is largely used in the manufacture of aniline colors but the bulk of its compounds is used in medicine. A small quantity is also used in photography—the iodides of silver, potassium, ammonium, and cadmium being used for this purpose.

The tincture of iodine is a mixture of iodine and potassium iodide dissolved in alcohol. Iodine dissolved in carbon disulphide gives a solution opaque to light but transparent to heat. To give the starch test the iodine must be in the free state and as it nearly always exists in combination, it is necessary to add to the liquid under examination some agent to liberate the iodine. The test is usually made by adding to the suspected liquid a little starch paste then a little chlorine water, the chlorine will liberate the iodine if present in the form of an iodide. Iodine is of course an equally delicate test for starch.

Iodine can be combined directly with hydrogen to form hydrogen iodide or hydriodic acid; this acid is very similar to hydrochloric and hydrobromic acids.

Oxides and Oxy-Acids of Iodine. Iodine can be directly oxidized by ozone but the only oxide definitely known is I_2O_5 . Iodic acid (HIO_3) has been isolated. The periodic acid (HIO_4) has not been isolated, but salts corresponding to the acid are known.

Other Compounds of Iodine. Iodine combines with carbon, nitrogen and boron forming compounds similar to the chlorine compounds of the same elements.

Considering the chemical resemblance of chlorine, bromine, and iodine it is very remarkable that the elements all combine with each other.

FLUORINE ; F.

Occurrence. Fluorine occurs in combined form as fluor-spar (CaF_2)—sometimes called Derbyshire spar on account of its abundant occur-

rence in Derbyshire. It is also present in the mineral cryolite a double fluoride of aluminum and sodium. In a small quantity it is present in a number of other minerals, in the bones, and in the enamel of teeth. Fluor-spar is the most abundant compound containing it. This mineral crystallizes in cubes or octahedrons with varying shades of color, some of which are very delicate and beautiful.

Preparation and Properties. Fluorine was not isolated until 1886. It was then obtained by decomposing hydrofluoric acid (HF) by electricity. It is a colorless gas and the most chemically active element known. On account of its intense disposition to combine with other elements, it resisted until recently all attempts to isolate it. It decomposes water instantly and combines readily with mercury. It explodes with hydrogen even in the dark, and combines with combustion with many non-metals, attacks the metals, and even attacks glass. No compound with oxygen is known.

Hydrogen Fluoride; HF. This is the most important compound of fluorine. The pure acid can be obtained by heating acid potassium fluoride in a platinum retort with platinum tube and condensing arrangement cooled by a freezing mixture. The acid thus obtained is a colorless liquid a little lighter than water. It has a strong affinity for water and produces a hissing noise when brought into contact with it. A solution of hydrofluoric acid in water is obtained by heating powdered calcium fluoride (CaF_2) with sulphuric acid, $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$. This operation is performed in a leaden retort with tube and condenser of the same metal, the condenser being cooled by a freezing mixture. This solution possesses powerfully acid properties and the vapor escapes rapidly from the water as the temperature rises.

The dilute acid dissolves all ordinary metals except platinum, gold, silver, mercury, and lead. It also readily attacks glass if the least moisture be present, though it has been found that the anhydrous acid does not affect glass.

Uses. The principal use of hydrofluoric acid depends upon its power of acting upon silica and the silicates. Powdered sand may be dissolved in the aqueous solution of the acid and if the solution be evaporated the silica will volatilize as silicon fluoride (SiF_4). If a silicate be digested and heated with the acid a fluoride of the base will be left.

The action of the acid upon glass is explained by its power of attacking silica, for glass is a mixture of two or more silicates.

A design may be etched or engraved upon glass as follows: let the plate be coated with wax or etching-ground and the design drawn with a pointed instrument cutting through the wax. The plate is then placed with the waxed side down over a shallow leaden dish which contains calcium fluoride and sulphuric acid. Upon the application of a little heat the acid is disengaged and speedily makes the impression

upon the glass. If the engraving is done with the vapor of the acid, the design is dull or opaque; if the liquid acid is employed the lines are transparent.

The gaseous acid does not produce an uniform opacity and is therefore not generally suitable for the purpose. For opaque etchings a solution of the acid fluorides of the alkalis is used, usually one containing some potassium or ammonium sulphate.

SULPHUR; S.

Occurrence. This is an elementary body of great importance. It occurs abundantly in the free state and also as a constituent in many combined forms. In the uncombined form it is usually though not invariably found in volcanic regions. In some localities sulphur is being deposited from chemical actions now taking place. These are called "living sulphur beds" and occur in the regions of geysers, hot springs, fumaroles, and other evidence of recent volcanic activity.

The free sulphur is also found disseminated through stratified deposits alternating with beds of clay or other minerals.

Sicily produces the greatest amount of native sulphur. It is also found in our own country in California, Nevada, Wyoming, Arizona, and Utah. The mines at Cove Creek, Utah, supply a considerable amount of sulphur. It occurs in many other places throughout the world.

In the combined form it occurs as the sulphide of many metals, the most important being iron pyrites, FeS_2 ; copper pyrites, CuFeS_2 ; galena, PbS ; zinc blende, ZnS ; and cinnabar, HgS . It occurs in sulphates and in hydrogen sulphide in many mineral waters.

It occurs in many natural sulphates, the most important being those of calcium, lead, strontium, magnesium, and sodium.

Extraction of Sulphur from Native Sulphur. *Lignation Process.* All native sulphur must be separated from the mineral impurities which accompany it. This is usually

done by the ^{qu}lignation process or melting out the sulphur and there are several ways of accomplishing this. The sulphur ore is sometimes made into a kiln and the sulphur is melted out by smothered combustion, a portion of the sulphur itself being consumed to furnish the heat. This method though wasteful as regards sulphur is cheap in other respects and is employed to a large extent. The heat for driving out the sulphur may be obtained from extraneous fuel. High pressure steam has also been employed for melting sulphur out of its ores; in this case the ores are subjected to the action of the steam in closed iron vessels. A solution of calcium chloride in water with boiling point at 120° C. is sometimes used for furnishing the heat to melt out the sulphur.

Distillation Process. The ores of sulphur are sometimes enclosed in retorts and subjected to distillation, the sulphur being condensed in the liquid state.

Purification of the Crude Sulphur. Sulphur obtained by any of the above processes usually contains a few per cent of earthy impurities from which it is freed by distillation. If the vapor of the sulphur is condensed in a chamber below the melting point, it gives a pale yellow powder known as sublimed or flowers of sulphur. When the temperature of the chamber rises sufficiently high the flowers melt and are run out into sticks giving the roll sulphur or brimstone. If the vapor of sulphur be conducted directly into a condenser kept cool, the sulphur is deposited in a liquid state giving brimstone which is said to differ slightly from that first named.

Extraction of Sulphur from the Sulphides. Sulphur was formerly obtained in considerable quantity from iron sulphide (FeS_2) by heating it in the absence of air. At a very high temperature nearly one-half the sulphur can be separated, but at ordinary furnace heat only about one-fourth is separated. This method of preparing sulphur has

practically ceased as a manufacturing industry, the pyrites being used for making sulphuric acid.

Sulphur can also be obtained from copper pyrites by roasting with proper precautions. This is sometimes done in the process of roasting the ore preliminary to the extraction of the copper.

The sulphur from the pyrites is generally found to contain impurities associated with those minerals and is purified by subsequent treatment.

Sulphur from Other Sources. Sulphur is obtained in some quantity from the waste products of the gas works and in still greater amount from the waste products of the alkali works. Its presence in these products will be explained subsequently.

Physical Properties of Sulphur. As ordinarily seen sulphur is a lemon yellow, brittle, crystalline solid, insoluble in water but soluble in carbon disulphide. It exhibits several allotropic modifications the two most characteristic of which are marked by their action with the same solvent—one form being soluble in carbon disulphide the other form not.

The soluble varieties of sulphur show two distinct crystalline forms; one the native form of sulphur is the rhombic octahedron, the same form which results when it crystallizes from solution; the other is the oblique prismatic which results when it cools after melting. The distinction between these crystalline forms extends to their fusing points and their specific gravities, the first having the higher specific gravity but lower fusing point.

The insoluble form of sulphur shows several uncrystalline varieties, the most important of which are the ductile and the amorphous. The ductile sulphur results when boiling sulphur is poured in a thin stream into water; it is soft and elastic like rubber. The amorphous sulphur is always formed when the flowers of sulphur are deposited and will be left undissolved if the flowers be treated with carbon disulphide. Milk of sulphur is a soluble amorphous form of sulphur obtained by precipitation by the addition of an acid to an alkaline solution of sulphur. This form is white and milky in appearance and is a medicinal preparation. If a solution of sulphur dioxide be decomposed by electricity sulphur appears at the negative pole as an insoluble amorphous variety, while if a solution of hydrogen sulphide be electrolysed the sulphur appears at the positive pole as a soluble amorphous variety. For this reason the soluble varieties have been classed as electronegative and the insoluble as electropositive.

Chemical Properties. Sulphur possesses energetic affinities combining directly with a large number of elements. Many of the sulphides in atomic constitution correspond with the oxides of the same elements. Any modification of sulphur heated in the air or oxygen takes fire and burns with a pale blue flame producing sulphur dioxide. Finely divided sulphur, especially flowers of sulphur, is slowly oxidized in moist air yielding sulphuric acid.

Sulphur in a finely divided state will combine with some of the metals at ordinary temperature and at a high temperature it will combine with nearly all the metals and with all the non-metals except nitrogen. It can very readily be made to display electrical properties as may be shown by friction or by powdering in a dry mortar.

COMPOUNDS OF SULPHUR AND HYDROGEN.

There are at least two compounds of hydrogen and sulphur. The most important, hydrogen sulphide, is analogous in composition to water having the formula H_2S . The other, hydrogen persulphide, contains a larger proportion of sulphur. Its formula has not been definitely determined but is thought to be H_2S_2 though it may contain a larger proportion of sulphur. There are reasons for thinking that still more complex compounds exist.

HYDROGEN SULPHIDE; H_2S .

Occurrence. This gas is present in the waters of many springs, which has caused them to be called sulphur springs and such mineral water sulphur water. It is found in large quantity among the gases issuing from volcanoes. It is very generally present among the products which result from the putrefaction of organic matter containing sulphur, both animal and vegetable. The offensive odor of rotten eggs is mainly due to it and it generally contributes to the unpleasant odors from sewers and drains. The gas is also found among the products of the destructive distillation of coal and other organic substances containing sulphur.

Properties of Sulphuretted Hydrogen. It is a colorless gas with the odor of putrid eggs and faintly sweetish taste. It is liquefied by a pressure of seventeen atmospheres. Water at ordinary temperature dissolves about three times its volume. The aqueous solution is acid to test paper and has the taste and smell of the gas. The gas is readily combustible giving the blue flame of sulphur. When the supply of oxygen is abundant the products of the combustion are water vapor and sulphur dioxide— $\text{H}_2\text{S} + \text{O}_3 = \text{H}_2\text{O} + \text{SO}_2$ —and when mixed with oxygen in the proportions indicated, and ignited, the mixture explodes. If the supply of oxygen be limited some of the sulphur will be deposited.

In the presence of moisture and oxygen the gas is decomposed with the deposition of sulphur hence the solution of the gas in water can not be kept for a great while; light produces the decomposition. The gas acts as a poison if inhaled in large quantities and even when much diluted with air it gives rise to disagreeable symptoms.

Hydrogen sulphide is decomposed into its elements at a temperature a little above 400°C . Chlorine and bromine decompose it at ordinary temperature, removing the hydrogen and depositing the sulphur. On account of its ready decomposability hydrogen sulphide acts as a reducing agent, thus when heated with concentrated nitric or sulphuric acid the hydrogen is oxidized and the sulphur deposited.

Action with the Metals and Metallic Oxides. Many of the metals and metallic oxides act upon sulphuretted hydrogen in a manner resembling the action of the other hydrogen acids. With some of the metals as mercury, silver, and lead, this action takes place at ordinary temperature. When heated in the gas several other metals decompose it. It is because of its action upon silver that silver plate and other articles of silver often tarnish; silver egg spoons are blackened by the sulphur present in the eggs.

Hydrogen sulphide acts upon many metallic oxides form-

ing metallic sulphides and water according to the general formula, $MO + H_2S = MS + H_2O$.

Action of Hydrogen Sulphide with Metallic Salts. Hydrogen sulphide is one of the most valuable reagents in the chemical laboratory because of its disposition to act upon solutions of metallic salts. When hydrogen sulphide is brought into contact with solutions of metallic salts, characteristic precipitates are often formed. These precipitates are insoluble sulphides produced by the mutual decomposition of the dissolved salt and the hydrogen sulphide, some acid being produced at the same time due to the combination of the acid radical of the salt with the hydrogen liberated from the hydrogen sulphide. This action may be represented by the general equation, $2MR + H_2S = 2HR + M_2S$.

All metals are thus precipitated from their solutions provided their sulphides are insoluble in the products of the reactions—water and dilute acid. Those metallic sulphides which are soluble in or decomposed by dilute acid would of course not be precipitated by the reaction above indicated. Any metals whose sulphides are soluble in acid solutions, may be precipitated from the solutions of their salts by the use of an alkaline sulphide instead of hydrogen sulphide. The alkaline sulphide generally used for the purpose is ammonium sulphide $(NH_4)_2S$ and the action is indicated thus, $2MR + (NH_4)_2S = M_2S + 2NH_4R$. From this reaction it will be seen that no acid is liberated and if the metallic sulphide represented in the second member is insoluble in the products of the reaction, it will be precipitated.

The metals may accordingly be divided into three classes—1. Those whose sulphides are soluble in water; 2. Those whose sulphides are insoluble in water and dilute acid; 3. Those whose sulphides are soluble in dilute acids but insoluble in water and dilute alkaline solutions. The first class is not affected by hydrogen sulphide; the members of the second class are precipitated from a solution of their salts by hydrogen sulphide and those of the third by the addition of ammonium sulphide.

The sulphides of the different metals often have very characteristic colors, which taken in connection with reactions when treated with certain reagents, give the means of distinguishing and thus determining the metal present in a given solution.

The action of hydrogen sulphide with the oxides and salts of lead explains the discoloration of lead paint which so frequently occurs. Any paint in which lead is an ingredient is liable to discoloration by hydrogen sulphide due to the formation of lead sulphide. Paintings so discolored are sometimes partially restored by continued exposure to light and air, the lead sulphide being converted into lead sulphate. The presence of hydrogen sulphide in gas may be detected by moistening a paper with a solution of lead nitrate or lead acetate and exposing it to the action of the gas. The paper is blackened if a trace of hydrogen sulphide be present; if the gas be in solution it will immediately blacken upon the addition of a soluble salt of lead. In each case the dark color is due to the formation of lead sulphide. The converse of course holds, and the presence of lead in solution may be detected by the addition of hydrogen sulphide or any soluble sulphide.

Preparation of Hydrogen Sulphide. It may be prepared by the direct union of its elements but for laboratory purposes it is generally obtained by the action of sulphuric or hydrochloric acid upon iron monosulphide,



The gas is given off without the application of heat. Obtained in this way the hydrogen sulphide nearly always contains hydrogen due to the presence of free iron in the iron sulphide.

The pure gas may be prepared by heating antimony sulphide with hydrochloric acid, $\text{Sb}_2\text{S}_3 + 6\text{HCl} = 2\text{SbCl}_3 + 3\text{H}_2\text{S}$; in this method hydrochloric acid must be used for dilute sulphuric acid scarcely acts upon the antimony sulphide and

the concentrated decomposes the hydrogen sulphide liberated.

The salts of hydrogen sulphide form an important class of ores of the useful metals and their properties will be subsequently described.

COMPOUNDS OF SULPHUR AND OXYGEN.

Four oxides of sulphur are known—the dioxide, SO_2 ; the sesquioxide, S_2O_3 ; the trioxide, SO_3 ; and the persulphuric oxide, S_2O_7 . The first two are important, the last two are scarcely known in the separate state and will not be described.

SULPHUR DIOXIDE; SO_2 .

Occurrence. Sulphur dioxide occurs in the gaseous emanations from volcanoes and has been detected in the waters of certain volcanic springs. It is sometimes present in the air of towns or in the neighborhood of manufacturing works, in these cases resulting from the combustion of the sulphur of the fuel or by liberation in some chemical process. It has already been stated that sulphur dioxide is always the product of the combustion of sulphur in air or oxygen. It is removed from the air by oxidation and converted into sulphuric acid.

Physical and Chemical Properties of Sulphur Dioxide.

It is liquefied at ordinary temperature under two atmospheres of pressure. Its boiling point is -8°C . and it produces great cold by its evaporation. Water dissolves about 40 times its volume at ordinary temperature and the solution is believed to contain sulphurous acid but the acid has not been obtained in the separate state. Its formula shows it to be over twice as heavy as air. It extinguishes flame and is sometimes used to extinguish burning soot in a chimney, the sulphur being burned in the fire-place. It is a stable compound and not readily decomposed; at a high temperature it will combine with oxygen passing to sulphur trioxide. It is poisonous, causing death very quickly when breathed in a pure state and being injurious in even small quantity.

Preparation and Uses. In the laboratory sulphur dioxide is generally prepared by deoxidizing sulphuric acid by heating with copper or carbon,

$2\text{H}_2\text{SO}_4 + \text{Cu} = \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$; $2\text{H}_2\text{SO}_4 + \text{C} = \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{SO}_2$; the first is the more convenient method for all ordinary illustration.

As a general rule it may be stated that those metals which act upon sulphuric acid at common temperature liberate hydrogen while those which act only by elevating the temperature liberate sulphur dioxide. Owing to its great specific gravity the gas may be collected by displacement or may be collected over mercury.

USES OF SULPHUR DIOXIDE.

Sulphur dioxide is extensively used as a bleaching agent for wool and straw goods which would be injured by chlorine. The presence of water is necessary for the action consequently the goods are usually moistened and subjected to the action of the gas. The sulphurous acid in bleaching often appears not to destroy the coloring matter but to form colorless compounds with it, for the original color frequently returns after the lapse of time. In other cases the action appears to be due to the abstraction of oxygen from the dye leaving it colorless.

The solution of the gas in water is found to possess great deoxidizing power and it is thought to be due to the reaction between the sulphur dioxide and water by which hydrogen is liberated, the liberated hydrogen then abstracting the oxygen from the other body.

Sulphur dioxide still further resembles chlorine in that it is used as a disinfectant. Clothes and buildings are often fumigated by burning sulphur but its action in this respect has been over-estimated. It has also been used as an anti-septic or preservative as it prevents and stops fermentation. Wine and beer casks are sometimes treated with it to prevent

change in the fresh liquor introduced, and certain salts of sulphurous acid may be used for the same purpose.

Sulphurous Acid and Sulphites. The solution of sulphur dioxide in water is believed to contain sulphurous acid H_2SO_3 . This compound is not known in a free state but a large number of salts is known which can be obtained by treating the gaseous solution in water with bases. This fact justifies the conclusion that the acid exists and its salts indicate the formula H_2SO_3 . The acid characters of the compound are not strong and it is very unstable, soon passing to sulphuric acid. The salts are of course called sulphites and as the acid is bibasic there are two kinds. Sodium sulphite is largely used in the manufacture of paper, to destroy the excess of chlorine used in the bleaching.

Sulphur Trioxide, Sulphuric Oxide, Sulphuric Anhydride, SO_3 . The compound may be formed by the direct union of sulphur dioxide and oxygen, by passing a mixture of the gases through a tube containing finely divided platinum. It may also be obtained by gently heating fuming sulphuric acid as indicated by the equation, $\text{H}_2\text{S}_2\text{O}_7(\text{heated}) = \text{H}_2\text{SO}_4 + \text{SO}_3$.

Pure sulphur trioxide is a liquid at ordinary temperature. It crystallizes when cooled in long transparent prisms which melt at 14.8°C . It fumes in the air and the solid form soon deliquesces. The oxide combines violently with water forming sulphuric acid. A piece of the solid oxide dropped into water hisses similarly to a red-hot iron. It is decomposed by heat into sulphur dioxide and oxygen.

SULPHURIC ACID; H_2SO_4 .

Sulphuric acid is of fundamental importance both in the arts and sciences and, in fact, is the most important and useful acid known. It is a principal agent in the preparation of inorganic acids described already and of nearly all other acids. In a great majority of the arts and trades, sulphuric acid finds a greater or less application. The variety and extent of the demand for this acid makes its manufacture one of the most extensive and important of modern industries. Owing to the above facts theory and practice combine to perfect the process of its manufacture which has now reached a high state of perfection.

The other important inorganic acids are obtained from their salts but this one is mainly made from its elements—

built up from its constituents. The constituent raw materials most abundantly required in the manufacture are sulphur, oxygen, and water vapor the last two being essentially without cost.

The Leaden Chamber Process. The principal process employed depends upon the fact that sulphur dioxide in the presence of water vapor and certain oxides of nitrogen and the oxygen of the air, is converted into sulphuric acid. The fundamental reaction results may be expressed as follows— $3\text{SO}_2 + 2\text{HNO}_3 + 2\text{H}_2\text{O} = 3\text{H}_2\text{SO}_4 + 2\text{NO}$; $2\text{NO} + \text{O}_2 = 2\text{NO}_2$; $2\text{NO}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{NO}$ —the last two operations are continually repeated.

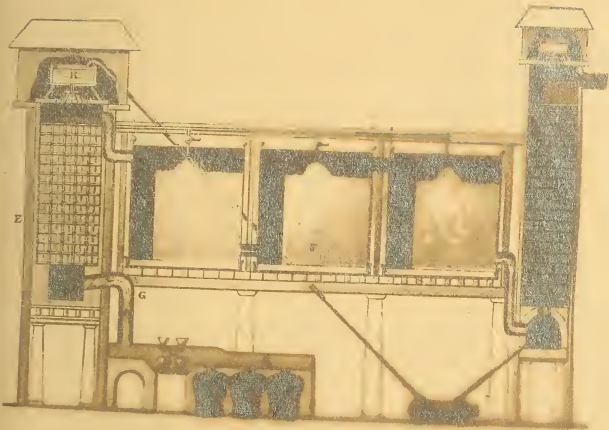
It appears that the nitric oxide acts as a carrier of oxygen taking it from the air and becoming nitric peroxide. By transfer of oxygen to the sulphuric acid the peroxide is reduced to nitric oxide and the operation is repeated continuously. If no loss of the nitrogen oxides occurred, a given quantity of nitric oxide would suffice to convert an indefinite amount of sulphurous acid gas into sulphuric acid but owing to unavoidable loss, it is necessary to constantly replenish this compound. This is usually done by generating a small quantity of nitric acid by the action of sulphuric acid upon sodium nitrate and the nitric oxide is produced as in the first of the above reactions.

The process of manufacture is as follows—Sulphur or metallic sulphides are burned in the air to produce sulphur dioxide. A small amount of the vapor of nitric acid is produced by the action of sulphuric acid upon sodium nitrate which vapor is caused to mingle with the sulphur dioxide and the oxygen of the air. To this mixture of gases in suitable apartments is added the proper amount of steam, when the reactions above indicated take place.

The plant employed in the process consists of 1st. The burner, in which the sulphur or sulphides are burned for the production of the sulphur dioxide. Through these burners is also admitted the air to

supply the oxygen required for the formation of the vitriol. 2nd, The arrangements employed for the production and introduction of the nitric acid vapor. These differ but that most generally used consists of a series of earthen ware or iron pots which are placed in the "nitre oven"; these pots receive the charge of sulphuric acid and nitre for the production of nitric acid. The "nitre oven" is usually a sort of receptacle in some part of the burner or its flues so that the heat from the burner promotes the evolution of the nitric acid and the vapor of the acid is carried along with the air and sulphur dioxide. 3rd, The chambers which are immense rooms completely lined with sheet lead. They vary in number and size, usually however there are three or four with a capacity of from 40000 to 80000 cubic feet each. Into these chambers the gases from the burners are introduced and at various points jets of steam are projected into them. The floors of the chambers are soon covered with a solution of sulphuric acid. 4th, In addition to the above mentioned parts of the plant there are supplementary appliances generally used, the most important of which are two towers. One situated between the burners and the chambers and the other at the exit end of the last chamber. The tower at the exit end of the chambers is to prevent the waste of the oxides of nitrogen, while the nitrogen of the air which takes no part in the chemical action in the chambers, is being removed therefrom. This exit called Gay Lussac's tower, is a tall chamber filled with porous material over which oil of vitriol is allowed to flow. The useless nitrogen escapes from the tower by a flue leading from the top of the tower to the chimney stack of the works but the oxides of nitrogen are absorbed by the oil of vitriol. The acid from this tower is pumped up and caused to descend over acid proof brick in another tower (Glover's), which is placed between the burners and the chambers. The hot gases from the burners also pass through Glover's tower and in so doing they take up the oxides of nitrogen from the "nitrous" vitriol and return them to the chamber. The hot gases from the burners in passing through Glover's tower also carry back steam into the chambers and thus save fuel in steam raising. In the Glover towers the production of sulphuric acid takes place to a greater extent than in any other part of the chambers of the same cubical contents. The towers are not in universal use but they accomplish great economy in the manufacture. When a Glover tower is used the whole of the chamber acid, as well as that from the Gay-Lussac tower, may be passed through it; the chamber acid is thus concentrated by the heat of the gases from the burners and the gases are themselves cooled to the required temperature.

If the chamber acid is passed through the Glover tower it has a specific gravity about 1.72 and is strong enough for many rough chemical manufactures. If the chamber acid is not sent through the Glover tower, it is taken from the chambers when it reaches the specific



Sulph acid

gravity about 1.60, for it then begins to absorb the oxides of nitrogen. This acid is strong enough for some applications but is usually further strengthened by heating in leaden pans until it reaches a specific gravity about 1.72.

The concentration can not be carried further in leaden pans because of the action of the acid upon the lead.

The acid of specific gravity of 1.72 contains about 80 parts of sulphuric acid and for greater strength the evaporation is carried on in glass, platinum or iron stills and this is the most expensive part of the operation. The concentrated acid of commerce thus obtained contains 98 parts of sulphuric acid and has a specific gravity of 1.84. The commercial acid generally contains some impurities, the most common of which are iron sulphate, lead sulphate, oxides of nitrogen, and arsenic. The last two may be removed by proper treatment and the first two by the actual distillation of the acid.

At a distance from the factories the cost of the acid is largely increased because of the risk involved in the transportation. In case of breakage or leakage in transportation it is a very difficult body to manage.

Pyrites now supplies the sulphur for much the larger proportion of sulphuric acid. In America the greater portion of the sulphur is from native sulphur, but the pyrites industry is constantly growing. The United States now produces annually about 750,000 tons of sulphuric acid. The greatest uses of the acid in this country are in the phosphate industries and in the refining of petroleum and manufacture of high explosives.*

* Mr. W. R. Quinan, Superintendent of the California Powder Works, informs the writer that certain advantageous improvements have recently been introduced in this country in acid manufacture. When pyrites is used as a source of sulphur it is almost impossible to obtain a perfectly clear acid, but by the improvements just referred to certain works have succeeded in producing a "sales" acid of 96 per cent strength in the Glover tower. This is done by lining the tower with very refractory material and greatly raising the temperature of the tower by conserving the heat from the burners. From the same authority it is learned that certain of the American works have succeeded in producing an artificial draught through the chambers by means of rotating fans placed in the flue at the end of the chamber system. This plan was first tried in Germany, but did not succeed then. This permits the production of a much greater amount of acid in the same chamber space. The acid chambers attached to the works above referred to yield three pounds of concentrated H_2SO_4 to each pound of sulphur burned.

Physical and Chemical Properties of the Acid. The concentrated acid obtained by the processes described always contains from one to two per cent of water. All the weaker acids by evaporation finally attain this composition and then distil over unchanged at the temperature of 338° C. The vapor evolved during the distillation is not that of sulphuric acid but is a mixture of sulphur trioxide and water vapor which pass over and condense together in the receiver. If pure, the acid is a colorless, heavy, oily liquid.

The acid has a powerful affinity for water and readily absorbs moisture from the atmosphere; for this reason it is often used as a dessicating agent. It is thus employed in the laboratory for drying without heat. The objects to be dried are placed over a dish of sulphuric acid in a closed vessel and the operation is greatly facilitated by exhausting the air from the vessel. The acid is also frequently used to dry gases, the gases being made to pass over a surface of the acid. Pumice stone soaked in the acid is admirably adapted to exposing the gases to the action.

The acid combines energetically with water, so that caution is always necessary in mixing them—the acid should always be poured into the water and not the reverse. The temperature produced by mixing the acid and water often exceeds that of boiling water. If four parts of the acid be added to one of powdered ice or snow there is an elevation of temperature, but if the proportions be reversed there is a reduction of temperature.

Owing to its affinity for water it decomposes many organic compounds containing hydrogen and oxygen, removing from the bodies these elements in the proportions to form water; it thus acts upon alcohol and oxalic acid. In a similar manner it acts upon paper, wood and sugar, removing the oxygen and the hydrogen in the proportion to form water and leaving the carbon in excess, with the result of charring the body. This action is finely illustrated in the

case of sugar as follows: Dissolve some crystalline cane sugar in three-fourths its weight of warm water and allow it to partially cool; then add a volume of concentrated acid equal to two-thirds of the volume of the water used, the liquid blackens and froths up as a spongy mass of carbon. Even when much diluted the acid corrodes and destroys textile fabrics.

Under the influence of heat it decomposes the salts of all acids more volatile than itself. On this account the acid is often said to be the strongest of the mineral acids, but this ability to decompose the salts of other acids is not alone the test of the strength of an acid as has already been pointed out.

At a red heat the vapor of the acid is decomposed according to the following reaction, $\text{H}_2\text{SO}_4(\text{heated}) = \text{SO}_2 + \text{H}_2\text{O} + \text{O}$.

Acids corresponding to the formula H_2SO_4 of 100 per cent purity can be obtained by adding to the concentrated acid the exact amount of sulphur trioxide to combine with the water there present. When the concentrated acid containing 97 or 98 per cent of sulphuric acid is cooled to -10°C . or below that point, the pure acid crystallizes and may be separated in the pure state; the latter process is now carried on upon a manufacturing scale.

In combining with water the acid forms several definite compounds the best known of which are the combinations resulting from the union of one molecule of acid with one or two molecules of water which may be respectively represented by the formulæ H_2SO_4 , H_2O and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$.

SULPHATES.

Sulphuric acid acts readily upon metallic oxides and carbonates converting them into sulphates in the latter case with the evolution of carbon dioxide. Sulphuric acid cold or hot, dissolves all the metals except gold and platinum. The boiling acid attacks silver forming the sulphate with evolution of sulphur dioxide. Under the same conditions it also acts slightly upon platinum. The very strong acid does not act upon cast iron. This metal can therefore be used for concentrating the acid after it reaches the strength which

attacks platinum. Before it reaches this strength it acts more readily upon iron than platinum. In the California powder works the last concentration takes place in iron retort, and Mr. Quinan states that *chilled* cast iron offers a high degree of resistance even to weaker acid. Gold is not acted upon hence the acid is often used in separating gold and silver or parting these metals. Generally speaking those metals which are acted upon at ordinary temperature by dilute acid liberate hydrogen, but when the concentrated acid or elevated temperature is required the corresponding sulphate is usually formed with the liberation of sulphur dioxide. This latter result is probably due to the decomposition of the strong acid by the liberated hydrogen, especially at high temperature.

The sulphates are an important class of compounds many of them being extensively employed in the arts. They are insoluble in alcohol; as a class they are soluble in water except those of lead and of the alkaline earth metals (calcium, strontium, and barium), and these are slightly soluble except that of barium which is absolutely insoluble in water and only slightly so in acids. The normal sulphates are decomposed by heat except those of the alkali and alkaline earth metals and of magnesium, the latter only partially decomposing at very high temperature. The insolubility of the barium sulphate gives a ready preliminary test for the detection of any sulphate in solution—which is to add to the suspected solution any soluble salt of barium and if any sulphate be present a white precipitate will be formed insoluble in water and dilute acid.

Pyro-sulphuric Acid or Di-sulphuric Acid. This acid is also called fuming sulphuric acid, Nordhausen oil of vitriol. Its formula is $\text{H}_2\text{S}_2\text{O}_7$ (H_2SO_4 , SO_3). It may be considered as consisting of a molecule of sulphuric acid and one of sulphur trioxide or two molecules of sulphuric acid less one of water. It is now made on a manufacturing scale by dissolving

sulphur trioxide in sulphuric acid. This acid was originally manufactured at Nordhausen in Saxony, a fact which explains one of its names. The original method consisted in distilling the basic ferric sulphate of iron by which sulphur trioxide was evolved and condensed in a solution of sulphuric acid. The basic salt being obtained by oxidizing ferrous sulphate by exposing it to a moderate heat in air. This acid fumes in the air when the bottle containing it is open, due to the escape of sulphur trioxide. It is heavier than the common acid, its specific gravity being 1.9. It has important application in the preparation of indigo dyes and in the colors obtained from coal tar. This acid was obtained by the last of the above processes as early as the fifteenth century.

Thiosulphuric Acid; $\text{H}_2\text{S}_2\text{O}_3$. It was formerly called hyposulphuric acid. This acid has not been obtained in a free state being very unstable.

Its salts however are stable and numerous, by far the most important being the sodium thiosulphate. This salt is simply prepared by digesting powdered roll sulphur with solution of sodium sulphite (Na_2SO_3). The latter salt combines with an atom of sulphur forming the thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) which may be crystallized from the solution. This is the salt so largely used in photography and commonly called hyposulphite or "hypo." It is also used as a substitute for sodium sulphite as an antichlore. The acid may be regarded as obtained from sulphuric acid by replacing one atom of oxygen by an atom of sulphur—hence the old term hyposulphurous is not strictly applicable.

Hyposulphurous Acid; ($\text{H}_2\text{S}_2\text{O}_4$). The solution of this acid has been obtained but it rapidly decomposes. Its salts are more stable than the acid. The sodium salt is the most important and is obtained by the action of zinc filings upon a concentrated solution of the acid sodium sulphite. This salt is used by the dyer and the calico printer and its formula appears to be $\text{Na}_2\text{S}_2\text{O}_4$.

There are several other oxy-acids of sulphur whose names and formulæ are here given, dithionic, $\text{H}_2\text{S}_2\text{O}_6$; trithionic, $\text{H}_2\text{S}_3\text{O}_6$; tetrathionic, $\text{H}_2\text{S}_4\text{O}_6$; pentathionic, $\text{H}_2\text{S}_5\text{O}_6$; very little is known of these and they are of little practical importance.

SELENIUM AND TELLURIUM.

Selenium. It is a rare element and much resembles sulphur in its mode of occurrence, physical and chemical properties. It has been found in the free state but in very small quantity associated with sulphur. It usually occurs as selenides of the metals together with the

sulphides. Selenium has been obtained in several allotropic forms the most distinct of which are the varieties which are soluble and insoluble in carbon disulphide.

The crystalline form of selenium is a conductor of electricity and this power is much greater in light than in darkness. This alteration of conducting power with variation of light intensity has been made use of in constructing the photophone but the instrument has not yet proved of practical value. The name Selenium is from the Greek word ($\Sigma\epsilon\lambda\eta\nu\eta$) for moon, the closely resembling element having been called tellurium from tellus the earth.

Tellurium. Tellurium is even less common than selenium. It has been found native in some gold ores, and in combination with gold and some other metals. It has recently been found in masses of 20 pounds weight in Colorado. It has the external appearance and lustre of bismuth and in its physical properties more closely resembles the metals than non-metals. In its chemical relations it is closely related to selenium and both these elements are connected by strong analogies with sulphur. Both tellurium and selenium form oxides and oxy-acids analogous to sulphurous and sulphuric oxides and the corresponding acids. They also form hydracids analogous to hydrogen sulphide, each of the above elements replacing sulphur in the respective compounds. Tellurium and selenium likewise combine with the chlorine group and notwithstanding their similarity to sulphur they both form sulphides.

PHOSPHORUS; P.

Occurrence. Phosphorus is very widely though not abundantly distributed in its compounds, but it never occurs in a free state. It is an essential constituent of all fertile soils. It is necessary to the growth of certain parts of the vegetable structures, especially of fruits and seeds. From plants used as food the compounds of phosphorus pass into the animal body and are essential constituents of the juices of the animal tissue, and more especially of the bony skeletons of animals which contain nearly three-fifths their weight of calcium phosphate. Its compounds are found in all sea water, generally in river water, and in many springs. It has also been found in meteoric stones. Phosphorus accordingly ranks with carbon, hydrogen, oxygen, and nitrogen as one of the elements essential to organic life. This element was discovered by Brand in 1668; he obtained

it from urine. Between 1670 and 1680 it is said to have been exhibited to several crowned heads of Europe as one of the wonders of nature. (Roscoe and Schorlemme, *Treatise on Chemistry*, vol. 1.)

Preparation of Phosphorus. Formerly phosphorus was entirely obtained from bone-ash, but now the greater cheapness of many of the phosphates of mineral origin has led to their use for the manufacture of phosphorus. Other things being equal bone-ash is still the most desirable raw material for obtaining phosphorus; the ash is tricalcic diphosphate $\text{Ca}_3(\text{PO}_4)_2$.

The essential chemical principles involved in the preparation of phosphorus may be stated as follows: The calcic phosphate is treated with sulphuric acid, which liberates the tribasic phosphoric acid with production of calcium sulphate. The tribasic acid under the application of heat loses water and becomes the monobasic acid. This acid is deoxidized by carbon with the liberation of phosphorus and formation of carbon monoxide. The changes are indicated by the reactions, $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 = 3\text{CaSO}_4 + 2\text{H}_3\text{PO}_4$; by drying at low red heat, $\text{H}_3\text{PO}_4 = \text{HPO}_3 + \text{H}_2\text{O}$; $2\text{HPO}_3 + 6\text{C} = 6\text{CO} + \text{H}_2 + \text{P}_2$.

The mechanical steps of manufacture may be outlined as follows—finely powdered bone-ash or other tricalcic phosphate is treated with sulphuric acid; the calcium sulphate thus produced is separated by filtration from the acid liquor, which contains orthophosphoric acid. This liquor is concentrated by evaporation in leaden pans. It is then absorbed by powdered charcoal, coke, or sawdust and heated to a dull red heat, by which action the orthophosphoric acid (H_3PO_4) is converted into meta-phosphoric acid (HPO_3). The mixture of meta-phosphoric acid and carbon is now distilled in clay retorts, when the phosphorus is separated and condensed under water which soon becomes warm and in which the melted phosphorus is conveyed to certain points from which it is removed.

NOTE.—By some authorities it is held that all the calcium is not removed by the sulphuric acid from the tricalcic phosphate but that the acid phosphate $\text{CaH}_4(\text{PO}_4)_2$ is formed which is dissolved in the acid liquid and converted into the metaphosphate of calcium by heat—

ing with carbon. This metaphosphate then liberates phosphorus when distilled with carbon.

The crude phosphorus thus obtained is purified by fusion and solidification and finally cast into sticks or wedges the entire operation being conducted beneath the surface of warm water. With unimportant exceptions the entire supply of the world's phosphorus is made at two places, Birmingham, England, and Lyons, France. To a small extent phosphorus has been produced in Philadelphia, Sweden and Russia.

Properties of Ordinary Phosphorus. Ordinary phosphorus when freshly made as above described is a translucent almost colorless wax-like solid. At ordinary temperature it is somewhat harder than wax, is flexible and sectile; at 5.5°C . and below, it becomes hard and brittle. Even in the dark it soon loses its translucency and becomes coated with an opaque white film. This action is hastened by the light, and by the action of direct sunlight it becomes red due to the conversion into the allotropic red phosphorus. It melts at 44°C . It is insoluble in water and usually kept immersed in that liquid. It is soluble in naphtha and carbon disulphide. It crystallizes when deposited from solution in carbon disulphide. Its specific gravity is 1.83 at 10°C .

Exposed to the air phosphorus gives off fumes and glows with a faint greenish light; both these phenomena are believed to be due to the oxidation of the phosphorus, but are not thoroughly understood.

It inflames in the air when heated above its melting temperature and burns with a brilliant white flame evolving white clouds of P_2O_5 . In pure oxygen this combustion is immensely luminous.

The low temperature of the ignition of phosphorus renders great care necessary in handling it to avoid accident. It should generally be manipulated under water. Ordinary phosphorus is very poisonous when taken internally. The

vapor is also poisonous when inhaled. Persons engaged in manufactures requiring the manipulation of phosphorus are often affected by phosphorus poison, very frequently resulting in the decay of the bones, especially those of the jaws and nose.

Phosphorus when moist will combine with oxygen, chlorine, bromine, iodine, sulphur, and with many of the metals.

Amorphous or Red Phosphorus. This is the principal allotropic form of ordinary phosphorus. When ordinary phosphorus is heated for 49 or 50 hours to 230° , or 240° C. in ovens, or in an atmosphere that does not act upon it, it is converted into a red opaque mass, which is widely different from common phosphorus. It is infusible at temperatures below red heat, is insoluble in carbon disulphide, is not poisonous, emits no vapor, and does not phosphoresce. It can not be inflamed by friction and does not even ignite in the air when heated to 260° C. at which temperature it is reconverted into ordinary phosphorus. The red phosphorus is much less chemically active than the ordinary phosphorus. This difference of action can be strikingly shown by placing the two varieties in contact with iodine when the red is unaffected and the common phosphorus unites with the iodine producing combustion. In the allotropic transformation there is no change of weight though the two varieties differ in specific gravity. The specific gravity of ordinary phosphorus is about 1.83, that of the red phosphorus is 2.14.

There are known other modifications of phosphorus. One form known as crystallized or metallic phosphorus can be obtained by heating red phosphorus in a sealed tube to 530° C. or common phosphorus may be heated to redness in a closed tube with lead for several hours. On cooling the melted lead the phosphorus crystallizes out in black sealy crystals. This form is more inactive than the red phosphorus. Professor Remsen describes a snow-white phosphorus obtained in the form of powder by cooling the vapor of phosphorus by ice-water in an atmosphere of hydrogen. The vapor density of phosphorus is 62 so that its molecule contains four atoms. At very high temperature the vapor density diminishes showing a tendency to correspond to the ordinary law of volumes.

Uses of Phosphorus. The principal use of phosphorus is in the manufacture of matches. It is also used to a small extent in the preparation of certain vermin poisons. The lucifer matches are made by tipping the splints with sulphur, wax, or paraffine, to surely convey the flame to the wood. The match composition consists of phosphorus and some oxidizing agent; those most commonly used being potassium chlorate, red lead, and lead nitrate. This mixture is usually bound together and attached to the wood by glue or gum.

The safety matches which can not readily be ignited by ordinary friction have no phosphorus on the match but are coated with a mixture of antimony sulphide and one or more oxidizing agents. For ignition the matches have to be rubbed on a prepared surface (usually the side of the box which is covered with a mixture containing red phosphorus; the red phosphorus mixed with fine sand or powdered glass).

Oxides and Oxyacids of Phosphorus. Four oxides of phosphorus are known the formulæ of which are— P_2O_4 , P_2O_5 , P_4O_6 , and P_4O_7 . The most important of these is the P_2O_5 phosphoric oxide.

Phosphoric Oxide. This oxide is prepared by burning phosphorus in dry air. It constitutes the white fumes which are seen when phosphorus burns with flame in dry air. It has a great affinity for water and soon deliquesces if left exposed to the air. It is sometimes used as a dehydrating agent in the laboratory. It will even extract water from oil of vitriol.

Orthophosphoric Acid; H_3PO_4 . This is the compound usually designated as phosphoric acid. It is the acid whose salts are usually met with in nature as phosphates. The phosphates are indispensable to the growth and sustenance of plants and animals. In these compounds phosphorus is widely distributed.

The acid is the final product of the oxidation of phosphorus in the presence of water. It may be prepared by boiling phosphorus with nitric acid. It can also be prepared from the native phosphates. The acid is tribasic. It was formerly used to a considerable extent in calico printing.

There are several other oxy-acids of phosphorus whose names and formulæ are given in the following table—

Hypo-phosphoric acid,	H_3PO_2 ;
Phosphorous acid,	H_3PO_3 ;
Meta-phosphoric acid,	HPO_3 ;
Pyro-phosphoric acid,	$H_4P_2O_7$.

Other Compounds of Phosphorus. Phosphorus does not combine directly with hydrogen but there are three compounds of these two elements known. The most important of these is the gaseous phosphuretted hydrogen, phosphine H_3P . This gas can be prepared in several ways and will generally take fire spontaneously when exposed to the air but this action appears to be due to the presence of the liquid phosphide H_4P_2 which is spontaneously inflammable. The other phosphide H_2P_4 is a yellow solid.

Phosphorus combines with the halogens forming two analogous compounds of each of the elements, chlorine, bromine, and fluorine. It also forms two compounds with iodine, but one of these is without an analogue among the other halogen compounds.

ARSENIC; As.

Occurrence. Arsenic occurs widely distributed but in small quantity, and resembles sulphur in its mode of occurrence. It is found native but more generally as the sulphides (realgar and orpiment) and the arsenides of the metals. It frequently occurs combined with the sulphides of the metals. Arsenic is used only to a small extent economically.

Preparation. It is generally prepared in one of two ways. 1. By heating arsenical pyrites out of contact with air, the arsenic is distilled off and condensed by suitable arrangements. 2. By heating arsenious oxide with charcoal, the oxide is reduced and the arsenic is volatilized and condensed.

Properties. In its appearance arsenic resembles a metal. It has a steel grey metallic lustre and is a conductor of heat and electricity. Its specific gravity is between 5 and 6. It volatilizes without fusing. In dry air at ordinary temperature it remains unchanged, but in finely divided form it oxidizes in moist air. At a temperature over 70°C . it oxidizes in the air and gives off fumes of arsenious oxide accompanied by a very penetrating and characteristic odor suggestive of garlic. When heated to a red heat in the air it burns with a bluish white flame, in oxygen its flame is very brilliant. It is insoluble in water. Pure arsenic does not appear to be poisonous but it may be oxidized after it is taken internally and then become a poison. In its chemical properties it is closely allied to phosphorus. Arsenic forms no base with oxygen and hence differs from the elements classed as metals. It is used in small quantities to form alloys which possess characteristic properties; it is thus used in the manufacture of shot, in bronzing brass and in other alloys.

OXIDES.

Arsenic forms two oxides, As_4O_6 and As_2O_5 .

Arsenious Oxide; As_4O_6 . This compound is prepared on a commercial scale by roasting arseniferous minerals in suitable furnaces or

ovens when arsenious oxide is the principal product; arsenical pyrites is usually the ore from which it is obtained. The sulphur and arsenic are thus oxidized the former escaping as sulphur dioxide. The arsenious oxide generally designated as "arsenical soot" is conducted into chambers which expose a large condensing surface. The oxide is here condensed to a dark grey powder.

The workmen employed to clear the chambers are clad in leather garments with glazed apertures for the eyes and they breathe through wet cloths. The powder is purified by resublimation and then obtained as a white, glistening, crystalline powder. If the crystalline arsenic be sublimed under slight pressure at high temperature white, amorphous, vitreous arsenic is obtained.

Arsenious oxide is obtained in large quantity as a bye product in working up certain volatile ores, mainly those of cobalt, nickel, silver, and tin. It is obtained in large quantities in connection with the tin furnaces of Cornwall and Devon.

The substance commonly known as arsenic in the shops is this oxide. It is usually sold in the form of a white powder resembling flour in appearance but much heavier its specific gravity being 3.7. It volatilizes without fusing. It may be distinguished from any resembling substance by the garlic odor emitted when dropped upon glowing coal. This odor is thought to be due to a lower oxide.

Arsenious oxide is a powerful poison, less than three grains have proven fatal. The habitual use of it in continually increasing quantities will enable the system to withstand much larger doses.

The best antidote for arsenic poison as given in the U. S. pharmacopœia, is a mixture of dilute solution of ferric sulphate and magnesia. Carbonate of soda may replace the magnesia and a solution of the perchloride of iron may replace the sulphate. Emetics should also be used as promptly as possible. This antidote was discovered by Bunsen in 1834. It was a deduction from known chemical facts. Previous to that time no antidote for this poison was known.

Arsenious oxide has many applications some of which will be mentioned.

Uses. It is used medicinally to a certain extent. It is sometimes administered to horses to render their coats smoother. It is used in calico printing and in the preparation of certain colors, arsenic being present in many pigments. It is used in the preparation of aniline, in glass making, as a constituent of white fire in pyrotechnics, as a preservative of skins, and in the preparation of various kinds of vermin poison.

Arsenious Acid. The acid has not been obtained in a free state. The solution of arsenious oxide in water, however, yields precipitates with certain metallic salts which indicate that the acid is tribasic, H_3AsO_3 . The brilliant Scheele's green is the arsenite of copper

(CuHAsO_3). The arsenites are insoluble or difficultly soluble in water, except those of the alkalies. The formulæ of the alkaline arsenites indicate that they are derived from HAsO_2 . Fowler's solution used in medicine is the arsenite of potassium.

Arsenic Oxide and Acid. This oxide can be obtained by heating arsenic acid. The acid is prepared by oxidizing As_2O_3 with nitric acid under proper precautions.

This acid is largely used as a substitute for tartaric acid in calico printing and in the preparation from aniline of rosaniline or the magnificent magenta dye.

Arsenetted Hydrogen ; H_3As . This is the only compound of arsenic and hydrogen known. It is always formed when nascent hydrogen and arsenious oxide are brought together in acid solutions. It is of importance because its production affords a means of detecting the presence of a very minute quantity of arsenious oxide. Marsh's test for detecting arsenic in cases of poisoning depends upon the production of the gas. The gas itself is exceedingly poisonous and any experiment with it should be undertaken with very great care. The chemist Gehlen lost his life by inhaling the gas.

Sulphides of Arsenic. There are known three sulphides of arsenic, the disulphide As_2S_2 , the trisulphide As_2S_3 , and the penta-sulphide As_2S_5 . The two first named occur native.

As_2S_2 , Realgar. This compound occurs native crystallized in red rhombic prisms. It may be prepared by heating arsenic with sulphur, or arsenious oxide with sulphur. The form which occurs in nature under the name of realgar, red orpiment, is usually prepared by distilling iron pyrites and arsenical pyrites together when the realgar distils over. It is used in the manufacture of the Bengal signal lights and Indian fire. In the air it burns with a blue flame; with nitre it gives a brilliant white light.

The Bengal lights are composed of a mixture of 24 parts of potassium nitrate, 7 of sulphur, and 2 of realgar.

As_2S_3 , Yellow Orpiment. This compound occurs native crystallized in yellow rhombic prisms. It may be prepared by heating arsenic with the proper amount of sulphur.

The paint known as King's yellow is a mixture of yellow orpiment and arsenious acid and is of course poisonous.

The penta-sulphide is of less importance than the other two.

Compounds of Arsenic with the Halogens. Arsenic forms but one chloride, the trichloride AsCl_3 . It forms analogous compounds with bromine, iodine, and fluorine. It also forms a dicarbide.

ARGON AND HELIUM.

Argon. This body was very recently discovered. Lord Rayleigh had found that the specific gravity of chemically pure nitrogen was not the same as that of the nitrogen of the atmosphere. This led to the examination of the atmosphere and to the discovery that it contained a substance not previously recognized, amounting to nearly one per cent. By the combined efforts of Lord Rayleigh and Professor Ramsey the substance was isolated in 1894. The new body was named Argon (signifying without work) in allusion to its chemical inactivity. The investigations up to this time indicate that Argon is an element with density of 20, referred to hydrogen. It appears to be mon-atomic and hence its atomic weight would be 40. It has been liquefied and solidified by great cold and pressure. It has, up to this time, resisted all attempts to cause it to combine with other bodies. As there have been very extended efforts to form a compound with Argon, with negative results, Professor Ramsey thinks that it may be non-valent or incapable of forming compounds.

Helium. The existence of this body has been inferred for a considerable time, through the existence of a bright line in the solar spectrum, not attributed to any known body. In seeking for a combined form of argon, Professor Ramsey for the first time in 1895 identified Helium among terrestrial bodies. It has not yet been definitely decided whether the body is an element, or a compound, or a mixture. The body is gaseous and has resisted all attempts to liquefy it although it has been subjected to enormous pressure and to the greatest attainable cold. Its boiling point under atmospheric pressure, according to Olszewski, must be below -264° C. Helium, like argon, has resisted all attempts to form from it a compound with other elements.

CHEMISTRY OF THE METALS AND THEIR COMPOUNDS.

THE ALKALI METALS.

The most important elements of this group are sodium and potassium. The other members are lithium, rubidium, and caesium. The first two are abundant in nature and widely distributed. Lithium is widely distributed, but only in small quantity. The last two members of this group are still more rare. These elements are highly electro-positive and as already stated their hydroxides are powerfully alkaline and their salts are generally soluble. The elements are soft, silvery white metals all of which decompose water and the two last of the group take fire in the air.

POTASSIUM; K; 39.1.

Occurrence. Potassium is not found in a pure state in nature but it occurs abundantly as a chloride in combination with other chlorides forming immense deposits. In combination with silicon and aluminum, it is a common constituent of the igneous and metamorphic rocks. From these rocks, by disintegration, it passes into the soil and finally into the plants, of which it is an essential food ingredient.

From plants the salts of potassium pass into the organisms of animals. In plants it is mainly present as salts of vegetable acids.

Preparation. Potassium was first isolated by Davy in 1807, by decomposing the hydroxide by electricity, the potassium appearing at the negative pole.

The method of Davy for preparing potassium has long since been superseded. It is now prepared by deoxidizing potassium carbonate with charcoal. For a good yield the ingredients should be thoroughly mixed. An intimate mixture of potassium carbonate and charcoal is obtained by calcining potassium tartrate ($C_4H_5O_6K$) in a covered crucible and this method is generally followed in preparing the carbonate for deoxidation.

The mixture of potassium carbonate and carbon is distilled in iron retorts from which a short iron pipe leads to a receiver containing petroleum and kept cool by ice water. When the retort is heated to a high temperature the potassium distils over and condenses under the petroleum. The reaction occurring is indicated by the following equation, $K_2CO_3 + C_2 = K_2 + 3CO$. The metal thus obtained is not pure and has to be redistilled or subjected to other treatment to perfectly purify it.

Metallic sodium is now again being manufactured by electrolysis and it is probable that Davy's method for obtaining potassium by electrolysis may be reintroduced.

Properties and Uses. Potassium is a silver white metal, specific gravity of .865 and rapidly tarnishes when exposed to the air. It floats on water and takes fire when placed upon water or even upon ice. More properly speaking the potassium decomposes the water and the liberated hydrogen takes fire, at the same time volatilizing some of the potassium, which burns with a violet color. Potassium melts below the boiling point of water. The greater difficulty attending the preparation of potassium and the fact that sodium can replace it in industrial operations has almost entirely limited its application to laboratory purposes. It will be seen from the relative atomic weights of potassium and sodium, that for equal weights, the latter element can do more chemical work.

Potassium Carbonate; K_2CO_3 . This important salt is obtained on a commercial scale by several different processes. Formerly most of the potash or crude carbonate was obtained from wood-ashes, but this source has greatly decreased in importance and now only parts of the United States, Canada, Russia, Hungary, and Galicia supply it from this source. The amount of the carbonate however from wood-ashes is greater than that from any other single source.

Potassium Carbonate from Wood-Ashes. It has already been stated that potassium exists in plants as the salts of organic acids. When the wood is incinerated the organic salts are decomposed and the potassium is left in the form of the carbonate. Of course the ashes contain other mineral substances resulting from other salts present in the plants. By lixiviation with water the more soluble salts are separated from the less soluble; the former consists mainly of potassium carbonate with considerable portions of potassium sulphate and chloride; ~~the former consist mainly of potassium sulphate and chloride.~~ By evaporation a considerable portion of the sulphate may be removed as it is less soluble than the carbonate. The residue then evaporated to dryness and calcined gives the crude potash of commerce which contains much potassium chloride and some sulphate. When greater care is observed in the process the product is purer and known under the name of pearlash.

Potassium Carbonate from Beet-Root Molasses. In making sugar from the beet-root there is left a syrup which can not be made to crystallize; this syrup is rich in mineral salts especially those of potassium. The syrup is first fermented for the production of alcohol. The liquor left behind is, in France, called "vinasse" and in German "schlempe." This liquor evaporated to dryness, calcined and the cinder lixiviated furnishes a high percentage of potash salts, K_2CO_3 , K_2SO_4 , and KCl. This industry has obtained great development in Germany and France.

Potassium Carbonate from the Chloride. A large amount of potassium carbonate is made from the native chloride by a process similar to that employed in the manufacture of sodium carbonate from common salt, yet to be described.

Potassium Carbonate from Sheep Wool. The washing from sheep wool is called "suint" and contains a considerable quantity of potassium mainly combined with animal acids. By evaporating the liquid to dryness and burning the residue the organic salts are decomposed and the carbonate of potassium left. This is separated by lixiviation from the ash.

The potassium carbonate is obtained from other sources in small quantity but not on a commercial scale.

Properties and Uses of Potassium Carbonate. The normal potassium carbonate is a white solid extremely deliquescent and soluble in less than its own weight of water, yielding a strongly alkaline solution. It is insoluble in alcohol. This substance is an important compound being used in the manufacture of soap and glass. In many States of America the country population make their own soap obtaining the potash from the ashes of the wood used as fuel.

The Acid Carbonate or Bicarbonate of Potassium. It can be prepared by passing carbon dioxide through moist potassium carbonate or through a solution of potassium carbonate. The salt is less soluble and less alkaline than the normal salt.

It is converted into the normal carbonate by heat, 2KHCO_3 (heated) $= \text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$. It is used to a small extent in medicine.

Caustic Potash; KOH. This substance may be prepared by adding a solution of slaked lime to a boiling dilute solution of potassium carbonate, $\text{K}_2\text{CO}_3 + \text{CaCO}_3 = \text{CaCO}_3 + \text{Ca(OH)}_2$ 2KOH ; the reaction will not take place if the solution of the carbonate be too strong. The solution decanted from the insoluble calcium carbonate and evaporated, leaves a clear

oily liquid which solidifies to a clear white mass on cooling. It is often fused and cast into slabs or sticks.

The hydroxide is a white solid, can be melted and volatilized, but is not decomposable by heat. It is deliquescent and readily absorbs carbon dioxide forming the carbonate, and is frequently used for removing carbon dioxide from gases. It is very soluble in water and evolves much heat in dissolving. It is powerfully alkaline being the most powerful alkali in general use. It softens and destroys the skin and on this account is used as a cautery. It is one of the most useful agents in the laboratory. Near ~~Stassfurt~~ *Stass* in Germany, caustic potassa is now produced in large quantity by decomposing a solution of potassium chloride by electricity. The works are primarily for the production of chlorine and the hydroxide is a valuable by-product.

Potassium Chloride; KCl. This salt was formerly obtained as a secondary product in the manufacture of bromine from sea water and of iodine from the ash of sea weed, and of sugar from beet-roots. It is now almost exclusively obtained from the mineral carnallite, which is a double chloride of potassium and magnesium, $\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$. Carnallite is found in vast quantities overlying the Stassfurt salt beds. The chloride is now an important raw material for manufacturing potassium carbonate and nitrate.

Potassium Iodide and Potassium Bromide; KI and KBr. These compounds are used to a considerable extent in photography, in medicine, and in the laboratory.

They are formed in the same way, by passing bromine or iodine into a solution of potassium hydroxide.

Nitre; Saltpetre; KNO_3 . This important salt is often found as an efflorescence upon the surface of the soil in hot dry climates. It results from the oxidation of nitrogenous organic matter in the presence of potash in the soil. The formation of nitre under these circumstances is due to the presence of specific microbes and the nitrification does

not take place without them. Nearly all of the native saltpetre in commerce comes from the East Indies, one of the districts of Bengal supplying the greater portion. It is chiefly found in the neighborhood of villages where the animal refuse supplies an abundance of organic nitrogen. The surface of the soil which shows the white efflorescence is scraped off and lixiviated with water. This solution evaporated to crystallization furnishes "crude nitre" in which form it comes into market.

This native process has been imitated artificially in the nitre beds or "saltpetre plantations." In Sweden formerly every land owner was obliged to furnish the government with a certain quantity of nitre. In France during the Revolution the artificial production of nitre was compulsory.

In the artificial process animal and vegetable refuse of various kinds are mixed with wood-ashes, calcareous earthy material, old mortar, bones, &c. This mass is occasionally moistened with stable drainings. After the lapse of the proper time watering is discontinued and salts soon effloresce on the surface of the heap. The surface layer to the depth of a few inches is then removed and the soluble salts dissolved out. The nitrates found in the solution are those of potassium, calcium, magnesium, and ammonium; the last three of which may be transformed into potassium nitrate by the addition of potassium carbonate to the solution.

In this process the basic parts of the nitrates except that of the ammonium nitrate, are derived from the earthy matters. The acid parts are believed to be formed by the oxidation of the ammonia resulting from the decomposition of the organic matter under the action of the "nitrifying" microbes. The presence of the bases is very favorable to the action.

Nitre from Chili Saltpetre. By far the greater portion of the nitre which now comes into the market, is made from sodium nitrate, NaNO_3 , by treatment with potassium chloride. Double decomposition ensues in accordance with the reaction, $\text{NaNO}_3 + \text{KCl} = \text{NaCl} + \text{KNO}_3$. The reaction is accomplished by boiling together equivalent quantities of strong solutions of the two salts. In accordance with the law of insolubility the least soluble salt at the boiling temperature (NaCl) is formed and precipitated. The crystallized sodium

chloride is removed from the hot solution and the liquid allowed to cool; during the cooling the salt least soluble in cold water crystallizes out (KNO_3). The solubility of the sodium chloride is about the same at boiling and common temperatures, so that there is no additional separation of it by cooling, while the solubility of the potassium nitrate is decreased more than six times by the reduction of the temperature.

Properties of Potassium Nitrate. Potassium nitrate crystallizes in six-sided rhombic prisms surmounted by six-sided pyramids. It has a cooling and slightly bitter saline taste. Heated above its fusing point it evolves oxygen and is reduced to the nitrite; at a still higher temperature the nitrite is decomposed with evolution of nitrogen and oxygen, leaving the oxide of the metal.

The salt is soluble in less than four times its weight of water at 18°C ., the solubility increasing very rapidly with the temperature; at 100°C . water dissolves nearly two and one-half times its weight of the salt.

Potassium nitrate, like the nitrates generally, is a powerful oxidizing agent. Its formula shows it to contain very nearly one-half of its weight of oxygen, five-sixths of which are available for the oxidation of the combustible body. It is chiefly used in the manufacture of gun-powder and pyrotechny.

Potassium Chlorate; KClO_3 . This salt is a white crystalline solid and like the nitrate is an oxidizing agent. It parts with its oxygen more readily than does the nitrate. At a high temperature it acts violently upon combustible bodies. If a jet of hydrogen or coal gas be placed upon the melted salt, ignition ensues and the gas burns brilliantly. The chlorate is much used in pyrotechny.

The common friction primers for firing cannon contain a mixture of the chlorate, sulphur and antimony sulphide

made into a paste with dissolved shellac. A pull on the lanyard withdraws a little rasp inserted in the primer and thus explodes the mixture, which ignites the powder in the lower part of the tube, and this communicates the flame to the charge in the gun. The fact that a mixture of it and sulphur explodes by friction prevents its use in the manufacture of gun-powder. Its use as an oxidizing agent in matches has already been referred to. By heat it is eventually decomposed into potassium chloride and oxygen, 2KClO_3 (heated) $=\text{KCl}+\text{KClO}_4+\text{O}_2$; $\text{KClO}_4=\text{KCl}+\text{O}_4$; for this reason it is the most convenient source for obtaining oxygen in the laboratory, as has already been stated. The chlorate may be prepared by the action of chlorine upon the hydroxide.

Potassium Sulphates. The normal sulphate occurs native associated with the sulphate and chloride of magnesium in the mineral karnite from which it may be readily separated. It is also produced as a bye product in several industrial operations. Karnite is used as a fertilizer and potassium sulphate is used in the manufacture of alum.

The bisulphate KHSO_4 , can be prepared by the action of sulphuric acid upon nitre. It finds use in chemical operations for decomposing minerals at high temperature, which are not readily attacked by acids; under these conditions its hydrogen gives place to metals.

OTHER COMPOUNDS OF POTASSIUM.

Oxides of Potassium. There are several oxides of potassium, the best known of which is K_2O_4 . This is the final product of the combustion of potassium in air or in oxygen. K_2O is thought to result when K_2O_4 is heated to a high temperature or when the hydroxide and potassium are heated together. The evidence of the existence of this oxide is deemed by some good authorities as unsatisfactory.

Potassium forms sulphides whose formulæ are, K_2S , K_2S_2 , K_2S_4 , K_2S_5 , and K_2S_7 . The compound KHS also exists.

SODIUM; Na; 23.

Sodium does not occur in a free state in nature. The most abundant natural compound of it is the chloride or common salt. Sodium, like potassium, in combination with silica and aluminum, is a common constituent of certain feldspars which go to make up many igneous and metamor-

phic rocks—it is not however so abundantly present in the rocks as potassium. Sodium also occurs abundantly in the native sodium nitrate.

The discovery of potassium naturally led Davy to the discovery of sodium which he also isolated in 1807 by a process entirely similar to that by which he obtained potassium.

Sodium is now manufactured in a manner similar to that described for potassium, namely by reducing the carbonate with charcoal, $\text{Na}_2\text{CO}_3 + 2\text{C} = \text{Na}_2 + 3\text{CO}$. By distilling a mixture of carbon and sodium hydroxide the reduction takes place at lower temperature; the sodium distils over and sodium carbonate remains in the retort, $3\text{NaOH} + \text{C} = \text{Na}_2\text{CO}_3 + \text{H}_2 + \text{Na}$. In Castner's method a mixture of iron and carbon is made by heating together tar and hæmatite iron ore, this mixture is sometimes called iron carbide, and is used in the process instead of charcoal alone as previously explained. The action of the iron is mechanical, serving to keep the carbon in contact with the fused hydroxide.

Metallic sodium is now manufactured in this country by the *Castner electrolytic process*. In this process the sodium hydroxide is decomposed by electricity. At this writing the details of process cannot be obtained.

Properties and Uses. Sodium is very similar in properties to potassium. It is silver white in color and at ordinary temperature can be cut like wax but below 0°C . it is hard. It is slightly lighter than water its specific gravity being less than .97 and will float upon that liquid. It decomposes water with liberation of hydrogen, but inflammation does not generally occur. If the water be warmed or the metal be placed on a slip of bibulous paper so that it will not move around, the temperature will rise sufficiently high to ignite the liberated hydrogen. The burning of the hydrogen volatilizes some of the sodium which gives a yellow color to the flame produced. Its action on water is not so energetic as that of potassium.

Freshly cut sodium is very lustrous but is immediately tarnished by exposure to the air. Sodium is a very important reducing agent, its principal application being in the preparation of magnesium, aluminum, and silicon from their chlorides. It also finds valuable application when amalgamated with mercury, such amalgam being more efficacious than mercury alone in extracting gold and silver from their ores.

Sodium Chloride ; Common Salt ; NaCl. Next to air and water this substance is the most essential to the life and health of the animal world. In addition to this it is one of the most important raw materials in the industrial arts. It is used in enormous quantities in the alkali industries and is the source of all the chlorine.

Occurrence. Sodium chloride occurs widely and is abundantly distributed. Immense deposits of it occur in various parts of the world. The waters of the oceans contain about three per cent of it—the waters of many lakes and springs are impregnated with it.

Preparation of Salt. In several countries salt is mined directly from the deposits. The most celebrated mine is that of Wielitzka, in Galicia, near Cracow. This mine has been worked for several centuries. It is also mined in Germany, in England, and at several places in the United States. Rock salt is mined in Louisiana, Kansas, and in Genesee, Wyoming, and Livingston counties, New York. Salt thus obtained is generally impure and is purified by solution and recrystallization.

The principal portion of the world's supply of salt is obtained by the evaporation of natural or artificial ~~mines~~ *brines*. Artificial ~~mines~~ are produced by admitting water to contact with the salt deposits and pumping it out after it has been heavily charged with salt. Both natural and artificial brines are often concentrated by exposing a large surface of the

liquid to the air, and this, in Europe, is accomplished by allowing the liquid to trickle over walls or towers of brush-wood. The concentration in suitable vessels is then continued by artificial or sun heat. In some places in this country the evaporation is mainly by sun heat alone, being carried on in shallow wooden vats. This is the process at Syracuse, N. Y., and in Bay and Saginaw counties, Michigan. At other places in these States the process is carried on entirely by artificial heat and known as the pan process.

In warm climates, France especially, considerable salt is obtained by the evaporation of sea water. This is accomplished in the marshes along the shore into which the water is admitted from the sea. As concentration is increased the liquid is let from one basin to another until it reaches the crystallizing area.

In cold countries salt is sometimes obtained from sea water by exposing the water in shallow pits and allowing it to freeze. A large portion of the water may thus be separated and the solution left may be strong enough to pay for evaporation by artificial heat.

In all these processes the purity of the salt depends upon the nature of the original brine and other salts are often obtained from the brines left (mother liquor), after as much common salt has been obtained as practicable. The size of the grain of the salt depends upon the temperature at which the crystallization takes place, the lowest temperature giving the largest grains.

Properties of Sodium Chloride. The properties of common salt are well known. Pure salt is very slightly deliquescent, the presence of magnesium and calcium chlorides greatly increases the tendency and they are often present in table salt. It is soluble in a little less than three times its weight of water at 0° C., and its solubility is very slightly increased by raising the temperature.

Sodium Carbonate; Na_2CO_3 . Preparation. Before the French Revolution this salt was obtained from the ashes of sea weeds. The necessities of the French nation led Napoleon to offer a reward for the discovery of some other method for preparing it. This appeal was answered by Leblanc in the discovery of a method of making it from common salt which not only cheapened the production of sodium carbonate but produced the most beneficial results upon many other manufacturing industries. It led to improvements in the manufacture of sulphuric acid; it cheapened the production of hydrochloric acid and chlorine for bleaching, thus benefitting the manufacture of all textile fabrics; it gave a tremendous impulse to the industries of glass and soap making.

Leblanc Process. A full description of a manufacturing plant can not here be attempted. Only the essential reactions involved will be given. The Leblanc process consists of three steps. 1st, The conversion of common salt into sodium sulphate by heating it with sulphuric acid, $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$; the sodium sulphate is called the salt-cake and the process the salt-cake process. 2nd, The conversion of the sodium sulphate into the carbonate by heating it with powdered coal and limestone, the reactions may be indicated by the reactions— $\text{Na}_2\text{SO}_4 + \text{C}_2 = \text{Na}_2\text{S} + 2\text{CO}_2$; $\text{Na}_2\text{S} + \text{CaCO}_3 = \text{CaS} + \text{Na}_2\text{CO}_3$ —the result of this process is called black-ash because of the dark color, from the carbon, of the mixture of calcium sulphide and sodium carbonate. 3rd, The last step in the process is the extraction of the sodium carbonate from the black-ash by lixiviation with water, evaporation to the crystallizing point, and calcination.

The salt thus obtained usually contains some common salt, some sodium sulphate, and some sodium hydroxide, the latter resulting from the action of the lime upon the sodium carbonate. To obtain pure carbonate the calcined soda is subjected to further treatment.

Solvay's Process. This process which has now largely replaced the Leblanc, depends upon the fact that if a solution of the acid carbonate of ammonium be brought into contact with a saturated brine solution double decomposition ensues, the less soluble acid carbonate of sodium being formed and crystallizing out, while ammonium chloride remains in solution. The result is accomplished by saturating a strong brine solution first with ammonia and then carbon dioxide, when the acid sodium carbonate is precipitated, $\text{NaCl} + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{NaHCO}_3 + \text{NH}_4\text{Cl}$.

By heat the acid sodium carbonate is converted into the normal carbonate, $2\text{NaHCO}_3(\text{heated}) = \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$. The CO_2 liberated in this operation is again used in the first step of the process. The NH_4Cl is decomposed by lime and the ammonia is used again, $2\text{NH}_4\text{Cl} + \text{CaO} = \text{CaCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O}$.

The manufacture of the carbonates by the Solvay process at Syracuse, N. Y., and at Saltville, Va., is now conducted on a large scale. Other extensive works for this process are being erected at Detroit and Cleveland.

From the reactions indicated in the above processes it will be observed that in the Leblanc method the sulphur is finally left combined with calcium forming calcium sulphide and in the Solvay process the chlorine is left combined with the same metal forming calcium chloride both of which products are of themselves worthless. This waste of raw material is a loss in economy of manufacture, and methods have been devised by which the sulphur and chlorine are recovered for continual use.

The carbonate is also prepared to a small extent from cryolite, which is a double fluoride of sodium and aluminum.

Properties and Uses of Sodium Carbonate. The normal carbonate crystallizes in oblique rhombic prisms containing ten molecules of water of crystallization ($\text{Na}_2\text{CO}_3 \cdot 10 \text{ Aq.}$). In dry air the salt effloresces and crumbles to a powder losing the

greater part of the water of crystallization; when heated all the water of crystallization is driven off. The carbonate is very soluble in water.

100 parts of water at 14° C. dissolve more than half their weight of the 10 Aq. salt. The solubility of this salt increases up to 36° C. but then decreases. At the boiling point water dissolves nearly four times its weight of the salt.

The salt is less soluble than potassium carbonate and is often called washing soda. It is made in enormous quantities for use in the manufacture of glass and soap.

The Acid Carbonate; Bicarbonate; NaHCO_3 . This salt is produced as described above in the Solvay process. It may also be produced by passing CO_2 into a solution or over crystals of the normal carbonate. It is used in medicine and quite extensively in the preparation of effervescing drinks.

Both these carbonates are found impregnating the waters of certain lakes. Lake Mono is an example in our own country.

Sodium Hydroxide; NaOH . This salt may be prepared by the action of lime upon a solution of sodium carbonate, the reaction being entirely similar to that for the preparation of potassium hydroxide, $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 = 2\text{NaOH} + \text{CaCO}_3$.

Sodium hydroxide is very similar to that of potassium. It is the form to which the carbonate is generally converted preparatory to its use in the making of hard soap, it is then called soda-lye. Caustic soda is now produced from common salt by electrolysis.

By the action of the electric current upon a solution of salt the chlorine is liberated and an amalgam of sodium and mercury formed. By mechanical means the amalgam is transferred to another compartment of the cell containing water, where the sodium is transformed into the hydroxide and the mercury returned to the first compartment for reamalgamation. In one compartment the mercury is the cathode and in the other the amalgam is the anode.

Sodium Nitrate; NaNO_3 . This salt occurs abundantly native associated with other salts, gypsum and common salt. It is found in enormous quantities in Chili and Peru and is known as cubic nitre or Chili saltpetre. It is purified by solution and crystallization. The pure salt is deliquescent and very soluble in water. The deliquescent property prevents its use in gun-powder but it is largely used in the manufacture of potassium nitrate and nitric acid.

Borax, Sodium Biborate; $\text{Na}_2\text{O}, 2\text{B}_2\text{O}_3$. This substance occurs as a native mineral under the name of borax or tincal. It is also obtained from other native borates. Tincal and other native borates are obtained in large quantities from the salines or marshes of southern California and Nevada. These marshes are remnants of former fresh water lakes. It also occurs abundantly in the waters of Clear Lake, California. In California true veins of calcium borate have been found and worked for conversion into borax. Borax may be made by acting on sodium carbonate with boracic acid and most of the borax of commerce is so made.

Borax is an acid salt and when fused dissolves many oxides forming glassy beads which often have characteristic colors. This action makes it valuable in blow-pipe tests in mineralogy—upon the same property depends its use for soldering metals. It is now used in considerable quantities in glazing porcelain and earthen ware and in making enamels.

Sodium Silicate. An artificial combination of sodium and silica has long been used under the name of soluble glass. It can be made by fusing sand and sodium carbonate together or boiling sand with a strong solution of caustic soda under pressure.

This glass is used to coat wood and render it fire-proof, for wall-painting, and frescoing and to make artificial stone. Sand moistened with it, pressed into moulds, dried, and highly heated gives an artificial sandstone, the sodium silicate fusing and acting as a cement. Any required color may be imparted by mixing the necessary metallic oxide with the sand.

Sodium Thiosulphite; $\text{Na}_2\text{S}_2\text{O}_3$. This salt is largely used in photography. It is commonly known as sodium hyposulphite or simply "hypo." It is formed as stated on page 149 by digesting sulphur with a solution of sodium sulphite, Na_2SO_3 .

Sodium Sulphates. There are sulphates of sodium corresponding to those of potassium. The normal sulphate $\text{Na}_2\text{SO}_4, 10 \text{ Aq.}$ known as Glauber's salt, is an intermediate product in the manufacture of the

carbonate. It has a bitter taste and is a strong purgative. The formula for the acid or bisulphate is NaHSO_4 , Aq.

Sodium forms several other compounds very similar to corresponding ones of potassium which will not be mentioned here.

AMMONIUM; NH_4 .

The similarity of certain ammonium compounds to analogous compounds of potassium and sodium has already been mentioned.

The compounds resulting from the action of acid oxides upon ammonia do not form these resembling salts until water is added. The true salts of ammonia are formed by the action of acids upon ammonia or by double decomposition. Many such salts are closely analogous to and isomorphous with those of potassium and sodium. In these salts the radical NH_4 is substituted for hydrogen and seems to play the same part as potassium and sodium in their respective compounds.

The above and similar facts have suggested the possibility of the existence of a compound metal which has been named ammonium. This radical NH_4 has never been isolated.

An experiment first made by Berzelius adds some weight to the supposition for the existence of a metallic radical. The amalgams of mercury have a metallic lustre while the compounds of mercury with the non-metals are without lustre. Berzelius produced what was thought might be an ammonium amalgam with the usual metallic lustre; the result tended to strengthen the belief in an ammonium metal. This amalgam may be produced by adding a little sodium amalgam to a solution of ammonium chloride*; a lustrous, porous, metallic-looking mass rises to the surface. This mass was once thought to be a true amalgam of mercury and ammonium, but it is now thought that the mercury is merely

*The sodium amalgam is readily prepared by adding a pellet of metallic sodium to a little mercury heated in a test tube.

inflated by the ammonia and hydrogen from the decomposition of the ammonium chloride. The mass soon subsides, ammonia and hydrogen escaping. The similarity of the ammonia salts to those of sodium and potassium is the strongest support for the theory of a compound metal and this similarity causes the description of the salts at this place.

SALTS OF AMMONIUM.

The salts of ammonium are derived almost entirely from the ammoniacal liquor of the gas works. This liquor contains an abundance of the carbonate and sulphide of ammonia. When the liquor is distilled with lime the more stable base expels the ammonia, which is then collected as may be desired.

AMMONIUM CHLORIDE AND SULPHATE.

These are the most common and important salts. To obtain the first the ammoniacal liquor is distilled with lime and the expelled ammonia is conducted into a vessel containing hydrochloric acid; to obtain the sulphate the gas is conducted into a vessel containing sulphuric acid; in each case the gas is absorbed by the acid and the chloride or sulphate formed and these crystallize from the acid. The chloride NH_4Cl is purified by sublimation and thus obtained as a tough, fibrous, and semi-translucent mass, difficult to powder. It has no odor but has a sharp saline taste; it is very soluble in water, with great reduction of temperature. This salt is valuable in medicine and for many other purposes and is the salt from which ammonia is generally obtained.

The sulphate $(\text{NH}_4)_2\text{SO}_4$ is manufactured in large quantity from the gas liquor and is generally purified by solution and recrystallization. It is largely used for the preparation of manures, of ammonia alum, and of other salts. A solution of it in ten parts of water is sometimes used to render

muslins less inflammable; muslins so treated will not burn with flame.

ACID AMMONIUM CARBONATE, SMELLING SALTS.

This salt is usually obtained by distilling a mixture of ammonium chloride and sulphate with powdered calcium carbonate and collecting the distillate. This commercial carbonate is a mixture of the acid carbonate NH_4HCO_3 and the carbamate $(\text{NH}_3)_2\text{CO}_2$. It is largely used in medicine and as a baking powder.

Sal volatile is an alcoholic solution of these salts. A strong solution of alcohol dissolves out the carbamate leaving the acid carbonate.

The normal carbonate is obtained from the commercial salt by treatment with strong ammonia.

AMMONIUM NITRATE.

This salt is prepared by adding ammonium carbonate to dilute nitric acid until neutralization has been reached. It can be made to crystallize like potassium nitrate; it is very soluble and is deliquescent, is easily decomposed by heat, and largely used in making nitrous oxide. It is a constituent of some explosives; Bellite contains it.

AMMONIUM SULPHIDE.

There are several sulphides of ammonium the most important of which is believed to have the formula $(\text{NH}_4)_2\text{S}$. It is a compound of great practical utility in the laboratory often giving very characteristic precipitates with the solutions of many metallic salts.

A solution of this substance is formed by saturating a solution of ammonia with hydrogen sulphide and adding an equal quantity of the ammonia solution, $\text{XH}_2\text{O} + \text{NH}_3 + \text{H}_2\text{S} = \text{NH}_4\text{HS} + \text{XH}_2\text{O}$; $\text{NH}_4\text{HS} + \text{NH}_3 = (\text{NH}_4)_2\text{S}$.

The ammonia salts are all soluble and volatile and can be decomposed at high temperature. They are readily

recognized by giving off ammonia when gently heated with lime, soda, or potash.

BARIUM, Ba.

Occurrence and Preparation. Barium occurs abundantly in nature as a constituent of heavy spar (BaSO_4) and witherite (BaCO_3); these minerals frequently occur in the gangue of lead mines. The metal finds no useful application; it is named from the great weight of its compounds (Barros, heavy).

It may be prepared by decomposing the fused chloride by the electric current. It is a yellow malleable metal and decomposes water at common temperature.

Barium Chloride; BaCl_2 . The chloride may be formed by dissolving the carbonate in hydrochloric acid and evaporating the solution. The solution of the compound finds frequent use in the laboratory.

Barium Sulphate; BaSO_4 . Barium sulphate occurs native abundantly as heavy spar. It is produced artificially as a precipitate whenever a soluble sulphate is brought together in solution with a soluble barium salt.

The sulphate is used considerably as a substitute for white lead under the name of permanent white. The native sulphate is not satisfactory for the purpose and the artificial is prepared from heavy spar by heating the powdered mineral highly in contact with carbon when the following reaction takes place, $\text{BaSO}_4 + \text{C} = \text{BaS} + 4\text{CO}$. The sulphide thus produced is soluble in water and may be used to precipitate the sulphate by the addition of dilute sulphuric acid. The artificial sulphate may also be prepared from the carbonate by acting upon it with hydrochloric acid and using a solution of the barium chloride thus formed to precipitate the sulphate, which is practically insoluble in water.

Barium Carbonate. The carbonate occurs native as witherite. It may be prepared artificially by precipitation, by adding an alkaline carbonate to a solution of the chloride or by passing carbon dioxide

through a solution of the sulphide prepared as above described. The carbonate is principally used in the preparation of the other salts.

Barium Nitrate; $\text{Ba}(\text{NO}_3)_2$. This salt is prepared by acting upon the carbonate or sulphate with dilute nitric acid and evaporating to crystallization. It is used as a constituent of certain explosives and in pyrotechny.

Barium Chlorate; $\text{Ba}(\text{ClO}_3)_2$. This salt is prepared by acting upon the artificial carbonate with a solution of chloric acid; it is used in pyrotechny. The salts of barium impart green color to flames.

Barium Hydroxide; $\text{Ba}(\text{OH})_2$. A solution of the hydroxide is used as a reagent in the laboratory. It is a delicate test for carbon dioxide, for it becomes turbid by a trace of the gas.

The hydroxide may be prepared by dissolving the oxide in water the oxide being obtained by heating the nitrate. On a large scale the hydroxide may be made by passing steam and carbon dioxide over the sulphide heated to redness and decomposing the carbonate thus produced by superheated steam; the results are indicated by the following reactions, $\text{BaS} + \text{CO}_2 + \text{H}_2\text{O} = \text{BaCO}_3 + \text{H}_2\text{S}$; $\text{BaCO}_3 + \text{H}_2\text{O} = \text{Ba}(\text{OH})_2 + \text{CO}_2$.

Barium Sulphide; BaS . It is prepared as above described. It has the property of shining in the dark after exposure to light, phosphorescent.

Properties of Barium Salts. Any soluble barium salt will give a precipitate insoluble in nitric acid, with the solution of any soluble sulphate; upon this action is based the use of the nitrate and chloride in the laboratory.

Alkaline carbonate or ammonium carbonate gives a white precipitate with the solution of a barium salt, insoluble in excess but soluble in nitric acid.

CALCIUM; Ca'' ; 40.

Occurrence. Calcium has not been found in a free state in nature, but it is an abundant constituent of several mineral compounds. Its compounds occur in many waters

and also abundantly in the animal and vegetable kingdoms. In the mineral kingdom its most abundant compounds are the carbonates, the silicates, the sulphates, phosphates, and fluorides; in organisms the compounds are mainly the phosphate, carbonate, and fluoride.

Preparation and Properties. Calcium was first prepared by Davy (1808) by the electrolysis of the chloride. It has a brass yellow color, is harder than lead, and is very malleable. It decomposes water at the ordinary temperature but not so readily as sodium and potassium. Its specific gravity is 1.58. It is not used in the metallic state.

Calcium Carbonate; CaCO_3 . This compound in varying degrees of purity, exists in great abundance throughout the world. It forms rocky beds of limestone (marble, chalk, &c.) of immense thickness and extent. It is the chief constituent of the shells of mollusks, of egg shells, and of coral formations. The wide distribution of this mineral and its slight solubility in waters containing carbon dioxide explain its presence in many waters which have already been described as hard waters. In its different forms it is widely used as a building stone for interior decorating, and for the preparation of lime. It is also used in the reduction of iron from its ores and in many other metallurgic operations.

Lime; CaO . No other metallic oxide is used directly so abundantly as lime. Lime is manufactured in enormous quantities by burning limestone—that is by decomposing the limestone by heat; $\text{CaCO}_3(\text{heated}) = \text{CaO} + \text{CO}_2$. The carbonate commences to decompose at a red heat, but the liberated carbon dioxide must be removed to continue the decomposition. The carbonate can not be completely decomposed in a covered crucible. Lime is made in very large quantities in many parts of the world by heating limestone in rudely constructed kilns. The kilns employed are of various forms but always so arranged that the escaping

furnace gases pass over the heated stone, this being necessary for the removal of the liberated carbon dioxide. In the older furnaces the fires are kept up two or three days and nights and then the furnace is allowed to cool and the lime raked out. In the modern *continuous* furnace there are two styles of furnace; in one alternate layers of limestone and fuel are introduced into the furnace at the top, and the burned lime is removed from below; in the other the fuel and limestone do not come into contact, there being furnaces for the former and separate chambers for the latter. The stone is introduced above as the lime is raked out below. In all cases the limestone is broken into fragments of the proper size, otherwise complete decomposition does not take place in the interior of the kiln. In the great fire in New York City in 1853 marble columns that had been subjected to an intense heat were found unchanged beyond three inches from the surface.

If the limestone contains much argillaceous or siliceous matter and has been too highly heated, it is found to contain glassy masses which refuse to slake; the lime is then said to be dead burnt or overburnt. If the lime slakes but feebly it shows that it contains foreign substances, silica, clay, &c., and is then said to be a poor lime. If the lime combines readily with water, largely increasing its volume ($2\frac{1}{2}$ times), evolves much heat, and crumbles to a fine powder, it is said to be rich or fat lime. Air-slaked lime has been slaked by the moisture from the air. The process is necessarily slow, during which time the lime absorbs carbon dioxide as well as water; such lime contains frequently one-half its weight of the carbonate.

Calcium Hydroxide; Slaked Lime; $\text{Ca}(\text{OH})_2$. This substance is formed as above stated by treating fat lime with water, $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$. The hydroxide is slightly soluble in cold water and its solubility decreases rapidly as the temperature increases. The solution is used in the

laboratory for absorbing and detecting carbon dioxide in gases. It is readily converted into lime by the action of heat.

Slaked lime is used for numerous and important purposes. Its greatest use is in the preparation of mortar and for this purpose it has been used from time immemorial. It is probably one of the first chemical compounds artificially prepared by man.

Ordinary mortar is made by mixing together slaked lime and sand. The hardening of mortar is due to the gradual conversion of a portion of the hydroxide into the carbonate. Not only does the mortar harden but the whole forms a compact layer, attaching itself firmly to the stones between which it is placed. It is probable that the silica also in time combines with some of the lime forming a silicate and binding the whole more firmly together.

A mortar which has been exposed for only a few years contains more unaltered hydroxide than one of longer exposure, for this reason structures of the middle ages display more solidity than more recent ones. The sand in mortar prevents excessive shrinkage and favors the penetration of the carbon dioxide. Unaltered hydroxide has been found in mortars of the Roman era.

Freshly plastered houses are often uncomfortably damp because of the moisture which comes from the walls. The moisture is due both to the water mechanically mixed with the mortar and to that set free chemically by the conversion of the lime into the carbonate, $\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$. The hardening of the mortar and the drying of the walls can be hastened by burning coke in open grates in the closed rooms.

NOTE.—At 60° F. it requires 800 parts of water to dissolve one part of the hydroxide of calcium, and at 212° F. it requires 1500 parts of water to dissolve one of the hydroxide; lime water always gives a precipitate when boiled.

Anhydrous Calcium Sulphate; CaSO_4 . This substance exists in considerable abundance in nature, occurring as a native mineral called anhydrite. It is of little importance and can not be applied to the uses which make the hydrous sulphate so valuable. The hydrous sulphate will now be described.

Hydrous Calcium Sulphate; Gypsum; $\text{CaSO}_4, 2\text{H}_2\text{O}$. This compound is met with in considerable abundance in nature and the many different varieties are included under the name of gypsum. Gypsum occurs in considerable abundance in natural beds. It is slightly soluble in water, being most soluble when the water is at the temperature of 35°C . (1 part in 400). It is this substance in solution which produces the permanent hardness of water, already referred to.

When gypsum is heated to near 200°C . it loses three-fourths of its water, $2 \text{CaSO}_4, 2\text{H}_2\text{O} = (\text{CaSO}_4)_2, \text{H}_2\text{O} + 3\text{H}_2\text{O}$; and then constitutes plaster of Paris so named because obtained in large quantities from quarries near that city. When the plaster of Paris is ground to powder and mixed with water to a paste it combines with the water to reproduce gypsum evolving heat, expanding, and rapidly setting to a hard mass. If the gypsum is heated to above 200°C ., all its water is driven off and it loses the property of taking it up rapidly again. Such overburnt gypsum is valueless for the use of the ordinary plaster.

The properties of the plaster give it many useful applications. It is extensively used in making moulds and casts, statuettes, copies of coins, medals, &c., for the interior finish of walls and ceilings, and for the plaster bandages of surgeons. Ten per cent of lime added to the plaster accelerates the setting and increases the hardness. If the plaster be moistened with a strong solution of alum instead of water the setting is delayed and allows more time for manipulation.

Stucco consists of plaster of Paris mixed with a solution of glue or gelatine; it solidifies more slowly and becomes

hard enough to polish. Stucco may be given different colors by mixing with various metallic oxides.

When plaster of Paris is exposed to moisture it regains part of its water and accordingly deteriorates in value.

Plaster of Paris (burnt gypsum) is also a valuable fertilizer, its action is thought to be due to its power of absorbing ammonia and volatile compounds of ammonia thus rendering them more available for plant food.

Calcium Chloride ; CaCl_2 . This compound is obtained as a bye-product in certain chemical operations. It may be readily obtained by acting upon pure calcium carbonate with hydrochloric acid and evaporating the residue to crystallization. The powdered crystals mixed with snow or ice are used for artificial production of cold. When the chloride has been highly heated (200°C.) it is very efficient in drying gases and thus finds frequent use in the laboratory.

Calcium Fluoride ; CaF_2 . This substance occurs as a natural mineral and is the most important source of hydrofluoric acid, already described.

Calcium Sulphide ; CaS . This compound has the property of phosphorescing after exposure to light like barium sulphide. It is one of the constituents of certain luminous paints. The phosphorescence is not due to oxidation, since it is shown in a specimen that has been hermetically sealed for more than a century. It is now believed that the phosphorescence is due to impurities and that chemically pure sulphide does not show it.

Other Compounds of Calcium. There are many other compounds and salts of calcium the most common of which are the phosphates and the silicates. Certain of these are natural minerals and are of great importance in economic mineralogy and geology.

Reaction of Calcium Salts. Solutions of calcium salts give a white precipitate with alkaline carbonates, insoluble

in excess of the carbonate but soluble in nitric acid. They give white precipitates with soluble oxalates, soluble in acetic acid.

MAGNESIUM; Mg.

Occurrence of the Element. Magnesium does not occur native but occurs widely distributed in the combined form in many minerals. The most important of these are the carbonates and silicates of magnesium, more or less pure. Serpentine and talc are examples of the latter and dolomite of the former. Dolomite ~~or magnesium carbonate~~ is a double carbonate of calcium and magnesium. It occurs in immense beds and in places forms entire mountain masses.

Preparation, Properties and Uses. The metal may be prepared either by electrolysis of the fused chloride or by the decomposition of the chloride with sodium. It is a silver white metal, is malleable, but is ductile at only high temperature. It is pressed into wire in a semi-fluid state and afterward flattened into ribbon, in which form it is generally used. Its specific gravity is 1.75. It melts at a little below a red heat and is easily volatilized. In dry air it retains its lustre, but in moist air it soon becomes covered with a gray coating of oxide, which prevents further action.

In the form of ribbon or wire it takes fire in the air a little above a red heat and burns with great brilliancy, producing the oxide (MgO). To insure the combustion the unburned portion must be kept in the flame of the burning part or in contact with other flame. There are lamps specially constructed to accomplish these results.

The magnesium flame gives a continuous spectrum, which is rich in chemical rays (rays of great refrangibility). Because of this property the light may be used for photographic purposes in the absence of sunlight. For photographic purposes it has recently been largely superseded by electric light. It is still used extensively for signal lights and in flash-light cartridges for instantaneous photography.

Magnesia; MgO . This is the only oxide of magnesium. It is always produced when magnesium is burned in air. It is a white light powder, infusible except at the highest temperatures, and almost insoluble in water. It is a strong base and neutralizes acids in the most complete manner, though alkalinity is not shown by the taste. The oxide finds frequent use in medicine. On account of its infusibility it is largely used in the manufacture of crucibles, cupels, and fire-bricks.

Magnesium Sulphate; $MgSO_4$; Epsom Salts. The magnesium sulphate, the form known as Epsom salts occurs in many mineral waters. It derives its name from the Epsom springs in England. It is abundant in Hunyadi water. This salt was formerly prepared by acting upon dolomite (double carbonate of calcium and magnesium) with sulphuric acid. The calcium sulphate produced being very insoluble is easily separated from the magnesium sulphate. By far the greater portion of the commercial sulphate is now prepared from the native sulphate of the Stassfurth salt beds. By exposing this native and nearly insoluble salt to the action of water it is converted into the soluble Epsom salts. The sulphate is used in medicine as a purgative, and largely as warp sizing in the cotton trade.

The composition of Epsom salts is expressed by the formula $MgSO_4, 7H_2O$. Of this water six molecules are removed at $150^\circ C$., while the remaining one is driven off at $200^\circ C$. The native salt of the Stassfurth beds called Kieserite has the composition $MgSO_4, H_2O$.

Other Compounds of Magnesium. There are many other compounds of magnesium among which may be mentioned the chloride ($MgCl_2$) and the hydroxide $Mg(OH)_2$. The former occurs in many natural waters and is an important source of the metal. The hydroxide is much used in Europe for extracting sugar from molasses.

The carbonate occurs as a natural mineral, magnesite and the silicate occurs in talc, serpentine, mica, and several other minerals. The phosphate of magnesium is present in small quantities in bones and in certain seeds. The borate also occurs in nature.

ZINC; Zn''; 65.

Occurrence. Native zinc has been reported from a few places (South Africa, Australia, and Alabama) but the reports lack verification. If found at all in the free state it is in very small quantity. It occurs quite abundantly as a constituent of certain natural compounds, the most important of which are the common ores of zinc—zinc oxide, ZnO ; zinc carbonate, ZnCO_3 ; zinc sulphide, ZnS .

The mineralogical names for these ores are for the oxide, zincite, for the carbonate, smithsonite or calamine, and for the sulphide zinc blende or sphalerite.

Metallurgy of Zinc. The extraction of zinc from its ores is simple in principle but owing to certain properties of the metal its reduction requires distinctive arrangements. Zinc is fusible and volatile at such moderate temperature and so readily combustible in air that its ores can not be reduced like those of the other common metals, in an open furnace—in such furnace the zinc would be volatilized and burnt.

If the ores to be used for the extraction of the metal are the carbonate and sulphide, they are first converted into the oxide. To accomplish this the carbonate is calcined to expel moisture and carbon dioxide. The sulphide is roasted for several hours with continual stirring during which the sulphur is oxidized to sulphur dioxide and passes off. In each case the ore is left in the form of zinc oxide.

The extraction of the metal from the zinc oxide is accomplished by heating it with charcoal in specially constructed vessels of fire-clay. These retorts are connected with suitable receivers of the same or different material in which the zinc is collected. The carbon removes the oxygen from the ore forming carbon monoxide which escapes. The zinc volatilizes and is condensed in the receiver, the reaction being $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$.

At the beginning of the operation before the receivers have become hot the zinc deposits as a fine powder known as

zinc dust. This dust is a powerful reducing agent and is used in the arts as well as in the laboratory. As the process progresses the zinc collects in drops and then in the liquid state and is removed at stated intervals. The zinc obtained from the furnace condensers is usually impure, containing small quantities of the other metals lead being the most frequent impurity. For purification the spelter is remelted and the lead separated by virtue of its great specific gravity.

In some of the modern furnaces the carbonate is introduced into the retorts without previous calcining; the carbon dioxide is driven off long before the temperature of reduction is reached in the retort.

There are other methods employed for extracting zinc from the poorer varieties of ore. They may be included under the term "wet" processes and are not suitable for description here.

Properties of Zinc. Zinc is a bluish-grey metal of well known appearance; it is a little lighter than iron the specific gravity being about 7. Under ordinary circumstances zinc is brittle, but between 120° and 150° C. it is malleable and may be rolled and hammered and after such treatment it retains its malleability when cold. At 200° C. zinc again becomes brittle.

Until the beginning of the century zinc was only used to form alloys because prior to that time the manner of making it malleable was not known. At a bright red heat zinc boils and volatilizes and if air be admitted burns with a bluish-green light producing zinc oxide.

Zinc is soon tarnished in moist air becoming coated with the oxide which is gradually converted into a basic carbonate. The coating tends to protect the zinc from other action and renders it more durable. Commercial zinc is readily acted upon by dilute acids and at the boiling temperature decomposes water.

Pure zinc is not attacked by boiling water and is scarcely affected by either dilute or concentrated hydrochloric or sulphuric acid. Nitric

acid and the alkalis attack pure zinc. Impure zinc amalgamated with mercury resists the action of the acids just as does the pure zinc.

Uses of Zinc. Zinc is one of the highly useful metals. On account of its greater durability it is largely used to coat iron. Iron coated with either zinc or tin is commonly said to be galvanized. Zinc while it lasts acts more perfectly than tin; when tin is used the protection is effective only so long as the surface of the tin is unbroken. As soon as the iron is exposed the oxidation proceeds more rapidly than if the tin were not there. A coating of zinc protects so long as the zinc lasts. The difference in the action of these two metals is due to their different electrical relations to iron. By the above use of zinc its durability is combined with the great strength of iron.

The coating of iron plates with zinc is accomplished by producing a chemically clean surface on the iron and then dipping it into melted zinc. The surface of the melted zinc is covered with sal-ammoniac which prevents the bad effects which would result from the zinc oxide there formed.*

Zinc melts at a low temperature and its castings take a sharp impression of the mould. For these reasons it is used for many structural purposes where ornament rather than strength is considered. It has thus found general application in some countries for the preparation of statuettes, monuments, and other objects of beauty which can be bronzed or given any desired color. The recent process of photo-engraving consumes a considerable quantity of specially prepared sheet zinc. Zinc is used to a considerable extent for roofing and gutters and in electric batteries. Zinc dust is used industrially and in the laboratory as a reducing agent.

Zinc forms useful alloys with many metals, the most

*The sal-ammoniac (NH_4Cl) dissolves some of the zinc forming zinc chloride with liberation of ammonia. The zinc chloride dissolves the zinc oxide and prevents any of it adhering to the iron.

important of which are brass (copper and zinc) and german silver (nickel, zinc and copper).

Zinc Oxide; ZnO . Zinc forms but one oxide, ZnO . The oxide occurs as a red mineral zincite. The native oxide is only used as an ore of zinc. The artificial oxide is formed by the combustion of zinc in air. The zinc fumes are led into condensing chambers and the oxide is deposited as a powder. It is a white tasteless powder usually called zinc-white. It is used as a paint and while it has not the covering power or body of white lead, it does not change color by the action of sulphuretted hydrogen, the sulphide of zinc being white. Zinc white is also used in pharmacy and in the manufacture of certain kinds of glass.

The oxide is a strong base readily acted upon by acids forming salts isomorphous with those of magnesium. When the oxide is heated it turns yellow but is white again upon cooling. It is insoluble in water and very difficult to fuse. The oxide may be formed by decomposing the artificial carbonate by heat, the latter being precipitated from a solution of the sulphate by means of an alkaline carbonate.

Zinc Sulphate; ZnSO_4 ; White Vitriol. The sulphate is prepared on a large scale by the oxidation of the native sulphide. The sulphide is roasted in air and the sulphate formed is dissolved out with water and crystallized. The sulphate has a disagreeable taste and is used medicinally as an emetic; it is also used in dyeing, in calico printing, and in the manufacture of varnishes.

The formula of the sulphate is $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. At 100°C . it loses all the water except one molecule. It requires a much higher temperature to expel this last molecule.

Zinc Chloride; ZnCl_2 . The chloride is prepared by acting upon zinc or zinc oxide with hydrochloric acid and evaporating to crystallization. It is very deliquescent and its solution will dissolve paper and cotton. If zinc oxide be dissolved in a strong solution of the chloride, the solution will dissolve wool and silk.

Burnett's disinfecting fluid is a solution of zinc chloride. It absorbs sulphuretted hydrogen and ammonia and other offensive gases resulting from putrefaction. It is effective in arresting the decomposition of animal and vegetable substances. The chloride is used as a caustic in pharmacy and to a certain extent in the weighting of cotton goods.

Other Compounds of Zinc. Of the other compounds of zinc, the most important are the carbonate and sulphide. Their occurrence and use as ores have already been mentioned. A hydrate of zinc $\text{Zn}(\text{OH})_2$ is precipitated whenever alkaline hydrates are added to solutions of zinc salts. A silicate and a phosphate of zinc occur as natural minerals.

Reactions of Zinc Salts. Caustic potash and soda and ammonia give a white precipitate insoluble in excess. Ammonium carbonate gives a white precipitate soluble in excess.

Hydrogen sulphide gives no precipitate with solutions of zinc salts when free mineral acids are present. With neutral solutions or with salts of the organic acids and zinc the sulphide of hydrogen gives a white precipitate.

Ammonium sulphide gives a white precipitate with solutions of zinc salts insoluble in caustic alkalies. This white sulphide distinguishes zinc from all other common metals.

ALUMINUM.

Occurrence. Aluminum has not been found in the free state, but it is a widely distributed constituent of many natural mineral compounds. These compounds are simple or complex silicates, and the most abundant and important are clay, felspar, and the micas. The felspars are constituents of many of the most common and important rocks, granite, gneiss, and others. By the natural decomposition of felspathic rocks clays of varying degrees of purity result, the purest form being known as kaolin. Pure kaolin is a hydrated silicate of aluminum. Common clay is kaolin mixed with sand and colored by iron oxide and other impurities. Another important and frequently occurring natural

compound containing aluminum as a constituent is cryolite, a double fluoride of sodium and aluminum. Aluminum sulphate in the form of alum is found in certain waters. Aluminum is one of the most abundant constituents of the earth's crust.

Preparation of Aluminum. Aluminum is now prepared mainly by electrolysis, especially is this the method in this country. A powerful electric current is sent through a bath of cryolite (a double fluoride of sodium and aluminum) in which aluminum oxide (Al_2O_3) is dissolved. The metal is deposited at the cathode, the cryolite being kept fused by the heat of the current. The alumina used is artificially prepared.

Until recently and still to a certain extent in Europe, aluminum was prepared by reducing the double chloride of aluminum and sodium with metallic sodium.

An electrical process for making aluminum alloy is used extensively in this country (Cowles' process). In this process the aluminum oxide is mixed with carbon and the mass subjected in a furnace to the passage of a strong current of electricity. Under the intense heat the oxide is reduced but to collect the metal in a single fluid mass, it is found necessary to add copper or iron to the charge of the furnace and the alloys of these metals are then obtained.

Properties and Uses of Aluminum. Aluminum is a remarkable metal in that its specific gravity is 2.56 and yet it possesses many of the properties of the most useful metals. It is a white metal not acted upon by dry or moist air at the common temperature. It is very sonorous and has great tensile strength. It is ductile and malleable and can be beaten into leaf like gold and silver, but it requires frequent annealing during the operation. It is a good conductor of heat and electricity. It fuses at 625°C. and contracts upon solidifying.

At high temperature it oxidizes in the air and in the form of foil will burn in the air. Water and steam at high temperature act upon it. Nitric acid scarcely acts upon it at all nor does dilute sulphuric acid. Strong sulphuric and hydrochloric acids act readily upon it. Organic acids do not affect it nor is it acted upon by mercury.

As the price of aluminum falls its use is constantly extending. In some countries many of the soldiers' equipments are made of this metal (cooking utensils, canteens, spoons, other parts of the mess outfit, buckles, &c.) and it is being experimented with for similar use in our service. A considerable quantity has been employed in Germany for cartridge cases to contain smokeless powder, aluminum being much less rapidly corroded than copper. It is found admirably adapted for certain surgical apparatus (tubes, suture-wire, supports, &c.). It can also be used to replace the more costly platinum in electric batteries.

In addition to these uses of the pure metal it is used as an alloy. The alloy with 80 parts of copper (aluminum bronze) approaches steel in strength. Other alloys of it are very strong and yet very light. For engineering^{ing} and surveying instruments the strong light alloys are admirably adapted.

Aluminum Sulphate; $\text{Al}_2(\text{SO}_4)_3$, Aq. This salt may be prepared by acting upon aluminum hydrate with sulphuric acid and evaporating. The sulphate is prepared upon the commercial scale by acting upon clay with sulphuric acid. Clays (the hydrated silicates of aluminum) differ in their availability for the preparation of the sulphate. Bauxite is a variety of clay largely used for the purpose in England and in France. It is more easily acted upon by the acid but contains more iron than China clay or kaolin.

The sulphate is largely used for the same purposes as the alums which are next to be described. Indeed it is the presence of this compound in the alums that gives them their industrial uses. The common alum (double sulphate of aluminum and potassium) is preferable to the single sulphate for such uses because its crystalline form makes it

more difficult to adulterate and besides it is cheaper to prepare.

Alum: Double Sulphate of Aluminum and Potassium; $\text{AlK}(\text{SO}_4)_2$. Common alum is one of the most important artificial compounds of aluminum. This compound may be prepared by mixing solutions of the sulphates of potassium and aluminum and evaporating to crystallization.

Alum is generally prepared in one of two ways: 1st. By acting upon clay with concentrated sulphuric acid, by which aluminum sulphate is formed. Solution of this sulphate and that of potassium sulphate are then mixed in proper proportions and evaporated. 2nd. From alum shale, which is a shale impregnated with small crystals of iron pyrites. It also often contains bituminous matter sufficient to make it combustible. If the shale itself is not combustible it is mixed with some coal and made into long heaps. The piles of shale are then lighted and undergo a smothered combustion, which results in the formation of the sulphates of ~~potassium~~ *potas* *aluminum* and iron. These sulphates are dissolved out and mixed with solution of potassium chloride when double decomposition takes place between the iron and potassium salts with the formation of potassium sulphate and iron chloride. By evaporation the alum crystallizes from the solution. Potassium sulphate may be used instead of the chloride, but if there be much ferric sulphate an iron alum is formed which is isomorphous with and contaminates the potassium alum. The action in the shale heap consists in the oxidation of the iron pyrites with the formation of iron sulphate and sulphuric acid. The sulphuric acid attacks the clay forming $\text{AlH}(\text{SO}_4)_2$. In some cases with certain shales this action takes place by mere exposure to the air without any combustion.

A considerable amount of alum is also made from the natural mineral alunit. This substance may be considered as a basic alum with more alumina than the common alum.

By calcining and treating with water common alum is dissolved out, or by acting upon the alunite with sulphuric acid and adding the proper amount of potassium sulphate.

The alunite may be considered as a compound of one molecule of anhydrous alum and one of aluminum hydrate; it may then be represented by the formula, $\text{ALK}(\text{SO}_4)_2, \text{Al}(\text{OH})_3$.

Ammonia Alum. Ammonium sulphate may be used instead of potassium sulphate in the preparation of alum with the production of ammonia alum instead of potash alum. The two salts are entirely similar except that the first contains the radical NH_4 instead of K. This alum is manufactured at certain places where the ammonium sulphate is cheaper than the potassium sulphate. The ammonium alum answers equally ~~as~~ well as the potash alum in its most important applications. At one time in England large quantities of this alum were made.

Alum is very largely used in the preparation of pigments, as a mordant in dyeing and calico printing, in paper making, in clarifying water, and in the preparation of leather. Burnt alum which is used medicinally is prepared by heating common alum to a dull red heat driving off the water of crystallization.

Alumina; Aluminum Oxide; Al_2O_3 . Alumina is found in nature as corundum, a mineral next to diamond in hardness. Emery is an impure form of alumina. The ruby and sapphire are composed of nearly pure alumina.

Alumina may be prepared artificially by strongly heating ^{ammonium} common alum; it is left as a white insoluble powder. Alumina is a very weak base so that its salts may exhibit acid properties.

Aluminum Hydroxide; $\text{Al}_2(\text{OH})_6$. If solutions of aluminum salts (alum may be used) be treated with ammonia or alkaline carbonate, a white gelatinous precipitate is formed which may be dried to a soft friable mass. This hydroxide has a very powerful attraction for organic matter and when digested with solutions of vegetable coloring matters it com-

bins with and carries down the coloring matters leaving the liquid clear if the hydroxide be in sufficient quantity. The compounds resulting from the combination of the hydroxide and the coloring matters are called lakes. The fibres of cotton may be impregnated with the hydroxide and may then be permanently dyed. The aluminum compound has affinity both for the fibre and the coloring matter. Bodies thus used to fix the coloring matters are called mordants, hence the use of aluminum salts as mordants. Other compounds of aluminum besides the hydroxide have this property and will be again noticed.

Other Compounds of Alumina. The silicates of aluminum form a large and important class of minerals as already stated. Among the less important compounds of this element are the chloride, fluoride, and sulphide.

Thallium. This element was discovered in 1861 by means of the spectroscope. Its discovery was among the first applications of the spectroscopic method. Thallium resembles lead in its physical properties, in the character of its sulphide, and of its haloid salts. It resembles the alkali metals in its soluble hydrate and carbonate. But its chloride is nearly insoluble in which it is related to silver, but because of the relation between its properties and its atomic weight it is classed with the aluminum group. None of its compounds have found useful application. Its salts are poisonous and impart a green color to flame.

IRON; Fe; 56.

Occurrence. Iron is the most useful of the metals. It is only rarely found in the metallic or pure state. Metallic iron is usually the chief constituent of meteorites, those metallic masses which occasionally fall upon the surface of the earth. Meteorites generally contain several other elements among which are nickel, cobalt, and chromium. Meteorites weighing as much as 20 tons have been found. Native iron has also been found disseminated in grains and in large masses through certain igneous rocks.

As a constituent of natural compounds iron is very widely diffused. It can be detected in nearly all rocks, in many

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The alunite may be considered as a compound of one molecule of anhydrous alum and one of aluminum hydrate; it may then be represented by the formula, $AlK(SO_4)_2 \cdot Al(OH)_3$.

Ammonia Alum. Ammonium sulphate may be used instead of potassium sulphate in the preparation of alum with the production of ammonia alum instead of potash alum. The two salts are entirely similar except that the first contains the radical NH_4 instead of K. This alum is manufactured at certain places where the ammonium sulphate is cheaper than the potassium sulphate. The ammonium alum answers equally ~~as~~ well as the potash alum in its most important applications. At one time in England large quantities of this alum were made.

Alum is very largely used in the preparation of pigments, as a mordant in dyeing and calico printing, in paper making, in clarifying water, and in the preparation of leather. Burnt alum which is used medicinally is prepared by heating common alum to a dull red heat driving off the water of crystallization.

Alumina; Aluminum Oxide; Al_2O_3 . Alumina is found in nature as corundum, a mineral next to diamond in hardness. Emery is an impure form of alumina. The ruby and sapphire are composed of nearly pure alumina.

Alumina may be prepared artificially by strongly heating ^{ammonium} ~~common~~ alum; it is left as a white insoluble powder. Alumina is a very weak base so that its salts may exhibit acid properties.

Aluminum Hydroxide; $Al_2(OH)_6$. If solutions of aluminum salts (alum may be used) be treated with ammonia or alkaline carbonate, a white gelatinous precipitate is formed which may be dried to a soft friable mass. This hydroxide has a very powerful attraction for organic matter and when digested with solutions of vegetable coloring matters it com-

bins with and carries down the coloring matters leaving the liquid clear if the hydroxide be in sufficient quantity. The compounds resulting from the combination of the hydroxide and the coloring matters are called lakes. The fibres of cotton may be impregnated with the hydroxide and may then be permanently dyed. The aluminum compound has affinity both for the fibre and the coloring matter. Bodies thus used to fix the coloring matters are called mordants, hence the use of aluminum salts as mordants. Other compounds of aluminum besides the hydroxide have this property and will be again noticed.

Other Compounds of Alumina. The silicates of aluminum form a large and important class of minerals as already stated. Among the less important compounds of this element are the chloride, fluoride, and sulphide.

Thallium. This element was discovered in 1861 by means of the spectroscope. Its discovery was among the first applications of the spectroscopic method. Thallium resembles lead in its physical properties, in the character of its sulphide, and of its haloid salts. It resembles the alkali metals in its soluble hydrate and carbonate. But its chloride is nearly insoluble in which it is related to silver, but because of the relation between its properties and its atomic weight it is classed with the aluminum group. None of its compounds have found useful application. Its salts are poisonous and impart a green color to flame.

IRON; Fe; 56.

Occurrence. Iron is the most useful of the metals. It is only rarely found in the metallic or pure state. Metallic iron is usually the chief constituent of meteorites, those metallic masses which occasionally fall upon the surface of the earth. Meteorites generally contain several other elements among which are nickel, cobalt, and chromium. Meteorites weighing as much as 20 tons have been found. Native iron has also been found disseminated in grains and in large masses through certain igneous rocks.

As a constituent of natural compounds iron is very widely diffused. It can be detected in nearly all rocks, in many

minerals, and is present in the coloring matter of common clay and soils generally. The oxides, carbonate, and sulphide of iron are found abundantly and constitute the ores of iron.

ORES OF IRON.

Ores of a metal are the natural compounds of this metal which are worked to obtain the metal. The ores of iron are the following:

Chemical Name.	Common or Mineral Name.	Composition.
{ Ferric oxide or { Iron sesqui-oxide,	{ Hæmetite or { Specular iron ore,	} Fe_2O_3 .
Ferroso-ferric oxide,	Magnetic oxide or magnetite,	Fe_3O_4 .
Ferric hydrate,	Limonite or brown hæmetite,	$2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$.
Ferrous carbonate,	Spathic ore, { Clay iron-stone { or black band,	} FeCO_3 .
*Iron bisulphide,	Iron pyrites,	FeS_2 .

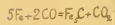
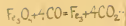
*The last is an ore of sulphur mainly but is sometimes worked for iron.

These ores frequently contain impurities. The spathic when mixed with clay is known as clay iron-stone, when with bituminous matter it is called black band. Other impurities are often present which must be wholly or partially removed in the manufacture. Compounds of sulphur and phosphorus are very often present and are very objectionable in the ores. Pyrites is seldom used as an iron ore but is more generally worked for the sulphur.

METALLURGY OF IRON.

This important branch of industry usually consists of two distinct operations. 1st, The production from the ores of a fusible carbide of iron (cast iron). 2nd, The conversion of the cast iron into pure iron (bar or wrought iron). Iron is however made direct from the ore.

Cast or Pig-Iron. Cast iron is made by subjecting the ores of iron to the action of reducing agents in a blast furnace but certain classes of ores often undergo a preliminary treatment before being introduced into the blast furnace.



Preliminary Treatment of Ores. This treatment consists in sorting the ore, breaking it into fragments of the required size, and subjecting the ore to a calcination or roasting process. The effects of the calcination are 1st, To drive off water when present in too large quantity. 2nd, To drive off sulphur, arsenic, and other volatile impurities. 3rd, To drive off carbon dioxide from spathic ores and to remove carbonaceous matter when there is an excessive amount in the black band. 4th, The conversion of the ferrous into the ferric oxides. 5th, The ore is left more porous and in better condition for the action of the reducing agents in the furnace.

This preliminary treatment is seldom applied to the hæmatite and magnetic ores unless they contain impurities. The calcination of the ore is often accomplished in open heaps or in rectangular chambers but in the most modern method the calcining is conducted in large circular kilns, the ore and fuel being charged in at the top—the process being continuous.

The Furnace. The furnaces in which the ore is reduced, differ somewhat in form and size depending upon the nature of the ore and fuel employed. The capacity of furnaces varies from 20,000 to 50,000 cubic feet, the best modern furnaces having between 15,000 and 30,000. The height varies from 40 to 100 feet, the most recent furnaces being not over 85 feet. Fig. shows a section of a modern American furnace, being that of one of the furnaces of the Edgar Thompson works. This figure also illustrates the manner in which furnaces are now supported, upon an iron frame resting upon piers. The furnace is jacketed throughout with plates of iron or steel riveted together; the furnace is lined with fire-brick, these being surrounded by common brick or stone. In nearly all modern blast furnaces the top of the furnace is closed by some such arrangement (cup and cone) as is shown in the figure. This serves to prevent the escape

of the gas from the top of the furnace and for the better distribution of the ore, fuel, &c., charged in at the top.

The heated gases are drawn off at the top by large pipes which lead from the furnace near the top above the stock-line—these pipes are known as “down comers.” The gases are used as a source of heat for heating the air fed to the furnace and for other purposes. Heated air is forced into the furnace through delivering tubes called tuyère pipes, one of which is shown at T in the figure. The temperature of the tuyère pipe is kept down by causing water to circulate through a truncated cone which surrounds it. Arrangements are always connected with the furnace for delivering the large quantities of raw materials which are introduced at the top. For introducing the materials the top of the furnace is entirely or partially surrounded by a charging gallery and the materials are carried up by some form of hoist or lift, unless the furnace is so situated that the gallery can be reached by bridge or trestle from higher ground. The slope of the furnace is that which experience has shown to be the best for the production and proper distribution of the required temperature conditions and for the proper movement of the materials charged into the furnace at the top and bottom.

The Fuel. The fuels used in blast furnaces are coke, anthracite coal, charcoal, and in certain localities some varieties of bituminous coal.

Reduction of the Ore. When the furnace is first started it is said to be “blown in.” For this purpose the furnace is charged with coke or coal, with wood at the bottom. A gentle blast is first employed so as to gradually raise the temperature and to produce regular expansion in drying and when the fuel has burned down to the proper distance there is introduced a charge of the iron ore mixed with flux (usually limestone) when the latter is necessary. Over this is placed a charge of fuel, then a second layer of ore and

flux, and so on in alternate layers until the furnace is full. It is usually several months before a full charge is employed in a furnace. The principal steps in the reduction in a coke furnace may be outlined as follows.

The hot blast from the tuyère pipes gives up its oxygen to the carbon of the fuel with which it first comes in contact producing carbon dioxide. The carbon dioxide is very quickly decomposed by the excess of red hot carbon forming carbon monoxide, so that at a very short distance (not over three feet from the tuyère pipes) no free oxygen or carbon dioxide are found in the ascending blast. At a short distance from the tuyères the gaseous current is composed of about $\frac{1}{3}$ carbon monoxide and $\frac{2}{3}$ nitrogen. The nitrogen is chemically inert but the carbon monoxide has great reducing power and as it comes in contact with the descending heated iron oxide it removes the oxygen from the oxide leaving metallic iron and forming carbon dioxide. This change takes place in what is called the upper reducing zone of the furnace and may be approximately stated as embracing the upper third of the furnace.

Just below this zone the carbon dioxide of the limestone is driven off.

The lime, clay, sand, and other impurities of the gangue, together with the metallic iron and coke, continue the descent, growing hotter and hotter. In this descent below the upper zone the principal and most important action which takes place is the removal of some of the carbon from the gaseous carbon monoxide with the production of carbon dioxide and the formation of iron carbide or cast iron. When the material of the furnace has descended to the level a little above that of the tuyère pipes a temperature is reached at which the silica reacts upon the lime and other bases, producing a slag composed of fusible silicates. It is in this region of the furnace that the oxides of silicon, sulphur, and phosphorus are reduced and these bodies enter

into the iron. The iron itself here reaches the fusing point and the entire charge is fused and flows down into the hearth, settling in two layers beneath the tuyère pipes, the slag on top. The region in which the oxides of silicon and phosphorus are reduced and the changes just referred to take place, is frequently called the lower reducing zone. For convenience in description we shall call the region between the upper and lower reducing zones the neutral zone.

There is an upper tap hole through which the slag is allowed to run off and the iron is drawn off at the lower hole at stated intervals. The slag, which has about six times the bulk of the iron, is made to run off to the most favorable point for removal from the vicinity of the furnace. The iron runs out into sand or iron moulds, forming rough cylindrical masses weighing about 100 pounds (called pigs) and the term pig-iron, as generally used, is synonymous with cast iron. The changes which take place in the different parts of a coke furnace may be summarized as follows: assuming the iron ore to be magnetite, this being the form to which all the ores pass soon after entering the furnace, then in the upper reducing zone the reaction is $\text{Fe}_3\text{O}_4 + 4\text{CO} = \text{Fe}_3 + 4\text{CO}_2$; in the neutral zone it is $\text{Fe}_3 + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2$; between the tuyères and the lower reducing zone the reactions are $\text{CO}_2 + \text{C} = 2\text{CO}$ and $\text{C} + \text{O}_2 = \text{CO}_2$.

The description above given for reducing ores applies to a modern coke furnace. When other fuel is used the shape and dimensions of the furnace are usually different and the reactions occurring in the furnace are somewhat differently distributed. By the use of selected ores and fuel and by special treatment in particular furnaces the nature and quality of the iron is under considerable control.

In the neutral zone as above designated it is pretty well established that the metallic iron takes oxygen from some of the carbon monoxide forming iron oxide and depositing solid carbon. At the high temperature of the lower reducing zone the solid carbon takes an active part in reducing the oxides of silicon, sulphur, and phosphorus. Some able

authorities assign much importance in this lower zone to the reducing action of the metallic cyanides which are known to be formed in the vicinity of the tuyère pipes.

Slag and Fluxes. All ores contain more or less extraneous matter and it would be impossible to separate the iron from these impurities unless they were brought to a liquid state. The extraneous matter after fusion constitutes the slag. If the impurities of the ore are not of such material as will fuse at the temperature of the furnace other materials are added to bring about this result; the added material is known as flux. The principle which governs the addition of the flux is that complex silicates are more readily fusible than simple ones. If the natural matter accompanying the ore usually called gangue, be clay (silicate of aluminum) limestone is added as a flux. This provides for the formation at the temperature of the furnace of a double silicate of calcium and aluminum which is more fusible than clay. If the gangue be silica, both clay and limestone are added the object being in each case to form fusible double silicates of aluminum and calcium. When silica is in excess in the slag there is too great a loss of iron by the formation of iron silicate.

It may in general be stated that for each ton of iron produced there is also a ton of slag and the bulk of the slag is about six times that of the iron. It thus becomes a serious problem in many places, to dispose of the slag produced at the furnaces. The slag is removed from the furnace in the most expeditious way and this of course depends upon the location of the furnace. It is often drawn off into bogies or trucks running on rails, the trucks being so arranged that the blocks of slag are easily removed when solidified. In this country at some furnaces side-tipping ladles lined with fire-brick are used to receive the slag, the ladle being mounted on trucks. With small furnaces the slag is usually run off into rough sand moulds from which it is removed when sufficiently cool.

Uses of the Slag. Slag has been used for macadamizing roads, especially when suitable stone is not readily obtainable, and for ballasting railways. Cast into blocks it has been used for break-waters, and occasionally for foundations of light structures; certain slags cast under proper conditions, have been used for paving blocks and for brick. The granulated slag which is produced by allowing melted slag to trickle into water, makes a good brick when mixed with $\frac{1}{11}$ its weight of lime and pressed into shape. The granulated slag ground to fine powder and mixed with lime yields an hydraulic cement. Slag wool or mineral wool is produced by blowing the melted slag with a jet of steam; this mineral wool is non-inflammable and a non-conductor of heat. The utilization of the slag is conducted on a large scale in Germany both in the production of brick and cement. In 1892 there were reported in that country ten slag-cement factories with a total production of 600,000 tons of cement. The slag run off from all the American furnaces during some of the most prosperous years would cover an area of a square mile to the depth of eight feet.

Furnace Gases. The gases which are led off from the top of the furnace through the "down comer" pipes besides being hot are highly inflammable. They consist of nitrogen (amounting to something over $\frac{1}{2}$ by volume), carbon ^{mon}oxide (about $\frac{1}{4}$ by volume), and carbon dioxide (about $\frac{1}{8}$ by volume). These gases are conducted off and used as a source of heat for generating power, or more generally for heating the air which is to be fed to the furnace. For the latter purpose the escaping gases from the blast furnace are conducted into suitable "stoves" or furnaces where the proper amount of air is admitted for the combustion of the carbon monoxide. The best modern "stoves" may be said to consist of a closed chamber containing a volume of brick-work so arranged as to expose a large absorbing surface to the heated gases. When the absorbing material of

the "stove" has become heated the furnace gases by suitable valves are shunted to another "stove," while the air to feed the furnace is driven through the first. The air to feed the blast furnace absorbs the heat given out by the gases which have already passed through the furnace. In this way the temperature of the blast can be raised to the desired extent. The blast frequently enters the tuyères at a temperature of 800 or 900° C. and under a pressure of from five to twelve pounds.

Some of the best chambers used to heat the blast contain brick so piled as to expose as much surface as possible—the Whitwell "stove" is divided by a series of partition walls in close proximity, built of fire-brick. The gases in their transit through the "stove" pass one wall at the top and the next at the bottom. In the Cooper "stove" hexagonal, honeycombed brick are stacked so as to make many flues through which the hot gases and air alternately pass.

These "stoves" may be used to heat gaseous fuel as well as the air for its combustion, when such fuel is employed. Gaseous fuel is ^{prepared} ~~preferred~~ for certain operations in a manner similar to that for preparing water gas and by the incomplete combustion of carbon; such gaseous fuel is generally known as "producer gas" and consists mainly of carbon monoxide. When the producer gas and air for its combustion are both raised in temperature by passing through the "stoves" and the "stoves" themselves heated by the products resulting from the combustion, it constitutes the system of "regenerative firing" and very high temperatures can be obtained.

From the above description it will be observed that the blast furnace is fed at the top with solid material, ore, flux and fuel, which form a continually descending column. It is fed at the bottom with air which continually passes upward in an ascending current. The total weight of the ascending current is about the same as the descending column. Some of the larger American furnaces use in 24 hours, 550 tons of ore, 450 tons of coal, 150 tons of limestone, and over 1000 tons of air. Such furnaces yield about one ton of iron for each ton of fuel.

COMPOSITION AND PROPERTIES OF CAST IRON.

The iron direct from the blast furnace is often designated as pig-iron; after remelting it is called cast iron. This dis-

tion is that of the foundry and not that of the laboratory. Chemically pig-iron is a particular variety of cast iron. Average cast iron contains from 90 to 95 per cent of iron, and from 2 to 5 per cent of carbon the remaining constituents generally being silicon, sulphur, phosphorus, and manganese—the silicon being the most abundant of these. Of these ingredients of the cast iron the carbon and sulphur are derived from the fuel, the silicon, phosphorus, and manganese from the ore.

There are two varieties of cast iron generally distinguished, viz.: white and grey. These varieties are based upon the condition of the carbon present in the solid metal. Fused iron dissolves and chemically combines with the carbon and if all or nearly all of the carbon is retained in combination after solidification, the metal has an almost silvery fracture and is known as white iron. On the other hand if a portion of the carbon separates from the iron on cooling in the form of minute graphitic like crystals, the metal will have a dark grey color due to the separated carbon—this form is the grey iron. A variety intermediate between these two is called mottled iron.

The difference of condition of the carbon in the white and grey iron is shown when specimens of each are dissolved in dilute sulphuric or hydrochloric acid. In the grey iron the separated carbon remains unaltered while in the white the constituent carbon passes off in combination with hydrogen giving some of the hydro-carbons having a disagreeable odor which is often observed when white iron is acted upon by acids.

The properties of the two varieties of iron are very different. The white iron is slightly heavier, is much harder, and fuses at a much lower temperature. The grey iron is soft enough to be cut in a lathe, and is more fluid when fused than the white and is therefore better for casting.

The condition of the carbon in the iron depends partly

upon the rate of cooling of the melted metal and partly upon the proportions of the other constituents present. Pure iron fused in contact with carbon is capable of combining with nearly five per cent of that element, but the amount of carbon that will be taken up depends upon the other constituents of the fused iron. Manganese increases the amount of the carbon dissolved by the iron while silicon and sulphur decrease the amount. In the cooling of the melted iron, manganese and sulphur tend to prevent the separation of graphitic carbon while silicon tends to cause this separation, accordingly white iron usually contains less silicon than grey.

If sulphur and manganese be present in the melted iron, it will more likely solidify as white iron. The effects of the manganese and silicon are the same both upon the melted and cooled metal but the sulphur tends to prevent the combination of the carbon with the melted iron and to cause it to combine with the solid iron. Phosphorus is thought to prevent the separation of graphite but to a less extent than sulphur.

The condition of the carbon in the solid iron can be materially modified by the rate of cooling. Rapid cooling prevents the separation of the carbon from the iron and slow cooling favors the separation, the first accordingly promotes the production of hard white iron and the latter that of grey iron. Chill-casting is brought about by virtue of the foregoing facts. Objects cast of soft grey iron may thus be made very hard externally by rapid cooling. If any particular portion of a casting is required to be hard the corresponding part of the mold is made of a good conducting material so as to rapidly cool that part. When white cast iron is melted and cooled very slowly it becomes grey.

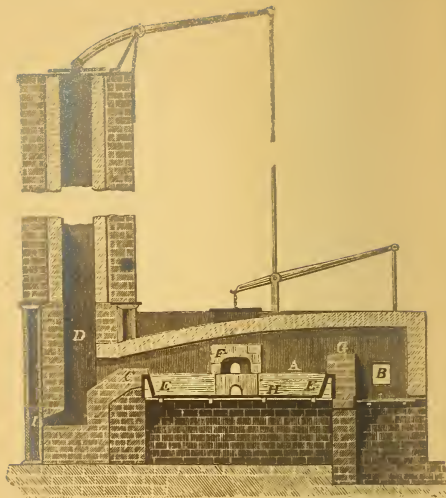
The varieties of cast iron, of course, grade into each other and it is difficult in every case to specify the variety to which a specimen belongs. For commercial purposes there are several grades of cast iron, the dark grey being number 1 and the hardest white iron being number 8.

Cast iron is the most fusible variety of iron. It is neither malleable nor ductile nor can it be tempered. It is hard and brittle, as already stated; it may contain as much as 7 per cent of other elements. Its tensile strength is small as compared with wrought iron and steel and its application for constructional purposes is much more limited than these latter. The white iron is generally used for conversion into malleable iron and the grey iron for foundry iron.

Wrought Iron. Wrought iron may be defined as commercially pure iron—it is not chemically pure as it contains something less than .15 per cent of carbon, with minute proportions of sulphur, silicon, and phosphorus.

Manufacture of Wrought Iron. Wrought iron is now made by two processes, 1st. By the direct process, that is directly from the ore; 2nd. By the indirect process, that is by the purification of cast iron. The indirect method is that most generally followed and will be first described. The principle of the more common process known as the puddling process will be given first.

Puddling. The puddling process is conducted in a reverberatory furnace in which cast iron is subjected to a purifying process, the carbon, phosphorus, sulphur, silicon, &c., being oxidized and removed. The general form of the furnace used is shown in the figure, the operation being conducted as follows: The bottom and sides of the furnace bed are covered with "fettling" consisting of slags rich in iron silicate or with such slags mixed with iron oxide. Five or six cwt. of pig-iron are charged into the furnace, the doors closed and the draughts turned on. When the iron is melted it is well rabbled or stirred so that every part of it is brought into contact with the oxide. Very soon the iron boils violently in consequence of the escape of carbon monoxide. After the boiling stage the metal "drops" or comes to "nature" and the whole mass becomes pasty. Slag



or tap-cinder is drawn off during and at the end of the operation.

The silicon, manganese, and phosphorus are separated mainly during the melting stage and pass into the slag. During the boiling of the iron the carbon is removed and also a further portion of phosphorus. The sulphur is eliminated in the slag in the form of iron sulphide.

The pasty iron is balled up by the puddler into masses weighing from fifty to one hundred pounds which are removed from the furnace and subjected to the action of a steam hammer. The hammering presses out the slag and causes the pasty particles of iron to cohere forming an oblong mass or "bloom." The "bloom" is passed through rollers and pressed into "puddled bars" but these bars are not yet fit for use. The puddled bars are cut up and made into bundles, reheated in the mill furnace, withdrawn at the welding heat, and passed through rollers until required dimensions are obtained. By this operation the texture of the iron is made more uniform, a fibrous structure imparted, and the quality generally improved. This product is commonly known as merchant bar. If the merchant bar be doubled upon itself, heated and rolled, it gives the "best iron bar" or wire iron. These operations improve the quality of the iron by pressing out more of the slag and appear to produce a slight chemical effect by removing by oxidation some of the impurities of the iron.

In the puddling operations just described the impurities of the cast iron are oxidized mainly by the oxide of iron used in the hearth though the oxygen of the air exerts some action and it is quite customary to add a little iron oxide or a mixture of iron and manganese oxides with the charge or after the metal has been melted. These also take part in the oxidation of the impurities. These puddling furnaces were originally lined with siliceous material but experience has led to the basic lining.

In this puddling process grey pig-iron is used because it becomes more liquid when fused. It is often spoken of as the pig-boiling process because the metal is so thoroughly liquefied and presents the appearance of violent boiling when the carbon monoxide is escaping. The whole operation usually occupies from one and a quarter to one and a half hours.

The puddling process was formerly and is yet sometimes preceded by a refining process. The refining consists essentially in subjecting the fused metal to a draught of air by which a portion of the iron is oxidized. The iron oxide reacts upon the impurities of the iron largely removing the silicon and sulphur and some of the phosphorus. The refined iron then remaining is puddled upon the hearth of a reverberatory furnace almost entirely similar to that used in the pig-boiling process. Formerly the impurities of the refined iron were oxidized largely by the oxygen of the air and the iron did not become liquid as in the pig-boiling process. It was therefore known as dry puddling. In dry puddling iron oxide latterly came into use to assist in the oxidation of the iron. The refining and dry puddling of the iron is not now generally practiced.

Mechanical Puddling. Owing to the heavy manual labor involved in the puddling operations described and to the desire to cheapen the process, several attempts have been made to effect mechanical puddling.

Dank's rotating puddling furnace (an American invention) was one of the most successful of these. The puddler consists of a large cylinder arranged to rotate about its horizontal axis. The inside of the cylinder is lined with "fettling," iron oxide, and lime. The flame gases from the heating furnace enter the cylinder at one end and pass out at the other. The cast iron to be puddled is run into the cylinder in a liquid state and the puddling is accomplished by rotating the cylinder by mechanical means. The results reached are brought about by the same chemical actions described in the pig-boiling process. This furnace has been gradually abandoned both in this country and Europe and is no longer in general use.

WROUGHT IRON DIRECT FROM THE ORE.

The earliest wrought iron was undoubtedly obtained direct from the ore and bar iron is still to a limited extent obtained in the same way. In these early methods the ore was heated in contact with the fuel under the action of the simple blast—in India to-day this method is followed, the air being blown in with a hand bellows. The American bloomery process is another example of a direct reduction process. The powdered ore mixed with charcoal, is heated on the open hearth of a bloomery furnace fed by a blast. In the processes just mentioned and in nearly all the direct processes the fuel used is charcoal. The methods as a rule are expensive and can only be followed where fuel and labor are cheap and special ores are accessible.

Eames' Process. Among the most recent methods of making bar iron may be mentioned that of Eames or the process of the Carbon Iron Company. In this process the iron ore is deoxidized in a reverberatory furnace which has a hearth lined with graphite or graphite mixed with some iron oxide. The iron ore is mixed with coke which has been treated with milk of lime (retarded coke) to diminish tendency to oxidation and placed upon the hearth of the furnace. The furnace is heated by natural gas and the reduction takes place at a moderate temperature.

When the ore is reduced the spongy metal is worked into balls and afterwards rolled into bars; or it may be charged while still hot into a bath of melted pig-iron on the open hearth of a steel furnace and ultimately converted into steel. This process has given satisfactory results in Pittsburgh and has passed to the commercial scale.

There are many other processes that have succeeded in obtaining iron direct from the ore but the Eames and the American bloomery process are the most important now operated in this country. The Eames process has not yet been adopted in Europe.

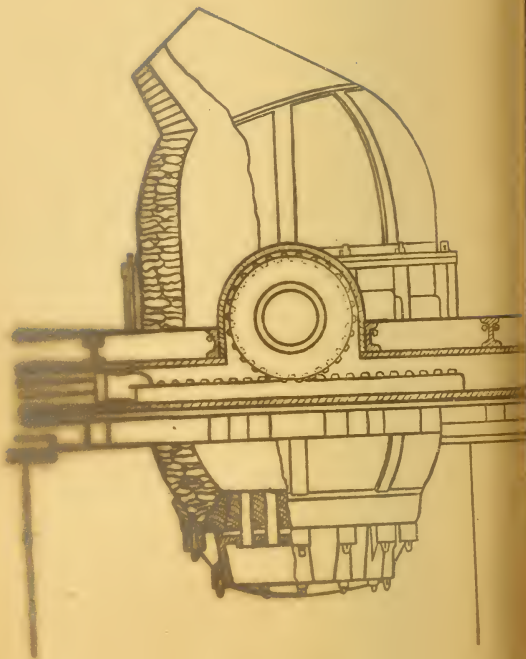
Properties of Bar or Wrought Iron. Wrought iron manufactured by the above described processes always contains some carbon and usually some silicon, phosphorus, and some sulphur. Chemically pure iron has neither the hardness nor tenacity of the commercial bar iron. Unless the amount of sulphur in the iron is very small it produces brittleness in the iron when it is hot, called red-shortness. An excess of phosphorus produces brittleness at ordinary temperature or cold-shortness.

The best wrought iron has a fibrous texture to which its tenacity is due. Such iron is very tenacious, ductile, and malleable. When the iron during its manufacture has not acquired the fibrous texture the strength is much less. Its strength is much greater in the direction of than across the fibres. It is thought that phosphorus in iron tends to cause large crystals preventing the fibrous texture and weakening the iron. The texture of iron is believed to have sometimes changed, gradually becoming granular and crystalline by frequent or long continued vibration.

At a red heat it becomes pasty and can then be readily welded and easily fashioned into shape. The smith usually sprinkles the heated metal with sand or borax to remove the oxide before hammering the surfaces to be welded together. The use of wrought iron for structural purposes, ship-building, armor plates, bridge construction, &c., has now been largely replaced by that of steel.

Manufacture of Steel. Steel in general contains more carbon than bar iron and less than cast iron. It is made either by purifying cast iron and then adding the necessary amount of carbon and other ingredients to form steel, or by adding carbon and other ingredients to bar iron. The first method is more generally employed in the manufacture of mild steel or ingot iron; the second in the production of hard steel.

The two principal processes in making steel from cast



iron are the *Bessemer* and *Open Hearth* processes. In the Bessemer process the decarburization and purification of the cast iron is accomplished by the oxygen of the air. In the Open Hearth process the oxidizing agent is mainly iron oxide.

The Bessemer Acid Process. In this process pig-iron melted in a cupola furnace or taken direct from the blast furnace is run into egg-shaped vessels known as "converters." The "converter" (fig.) is externally of iron and is lined with acidic or siliceous material and is arranged so as to rotate upon trunnions fixed on either side. Below the bottom of the "converter" is a blast-box, and several holes $\frac{1}{4}$ inch in diameter pass from the blast-box through the bottom of the "converter." The "converter" is turned into a horizontal position to receive the charge of from five to twelve tons of iron. The air blast is then turned on under a pressure of fifteen or twenty pounds and the "converter" rotated to an erect position. The air then passes up through the melted metal. The silica and manganese are then first oxidized with marked increase of temperature in the "converter;" then the carbon is oxidized to carbon monoxide which burns with a long flame at the mouth of the "converter." Some of the iron is also oxidized during the blow.

The oxidized silicon combines with the oxides of iron and manganese and rises to the surface of the metal as a slag.

When the carbon flame "drops" at the mouth of the "converter," it indicates that the operation is complete, that is, the carbon, manganese, and silicon have been removed from the iron.

The purified metal is then converted into the desired quality of steel by the addition of spiegeleisen or ferro-manganese to the melted charge just before it is poured. The ferro-manganese is a cast iron rich in carbon and manganese and of well determined composition; the ferro-manganese is always added in a fused state. The metal is allowed to stand

a few minutes after the last addition and is then poured into ladles and cast into ingots. The addition of the ferro-manganese not only gives the required hardness to the steel but the manganese counteracts the tendency to red-shortness.

The above was the original process and it will be observed that the "converter" was lined with siliceous or acidic material. It was found that the process could only be applied to iron fairly free from phosphorus for this objectionable constituent was but little removed by the operation.

The Bessemer Basic Process. The mechanical arrangements and general principles in the basic process are exactly the same as in that just described but the "converters" are lined with lime and magnesia (basic material) and lime to the amount of about 1-100 the charge of iron is put into the "converter" before the metal is run in. The "blow" is continued a little longer than in the original process and the oxidized phosphorus combines with the lime and is removed in the slag. By this modification in the original process it has become applicable to iron rich in phosphorus. The slag produced in the basic process is rich in calcium phosphate and is very valuable in agriculture. The basic process now finds wide application.

Open Hearth Steel. The Siemens-Martin process may be taken as typical of the open hearth methods. In the original method it was attempted to produce steel by melting together on the hearth of a reverberatory furnace cast and bar iron in the proper proportions. The method did not yield definite results and as now modified the Siemens-Martin process closely resembles in principle the original puddling process. The furnaces are similar to but larger than the puddling furnace and are lined with siliceous material. When the pig iron to be decarburized is melted appropriate quantities of iron oxide are introduced into the furnace. By thorough stirring the carbon, silicon, &c., are oxidized and removed

from the iron, the oxidation being accomplished mainly by the oxygen of the iron oxide but in part by the oxygen in the flame used to heat the hearth. After eight or ten hours the operation is complete but as in the Bessemer process the metal would be too soft for use. The required steely character is imparted to it by the addition of ferro-manganese to the metal as it is drawn off for casting. It is still customary in this process to add to the melted pig-iron waste scraps of bar iron and basic slag along with the iron oxide.

With the acid lined furnace in this process the same difficulty to a certain extent is experienced as with the acid Bessemer process; that is, to get the best results material free from phosphorus must be used.

The basic lining has accordingly been adopted in this process the chief modification being the substitution of a working bottom of basic material for the siliceous bed. As in the basic Bessemer process some lime is introduced with the charge and the process has been successfully applied to the phosphorus ores with every prospect of great extension.

The Siemens-Martin process is very generally operated by "regenerative firing" (page 203), by which high temperatures are produced and the purified iron easily kept perfectly liquid.

The steel produced by the Eames method already referred to comes under the head of open hearth steel.

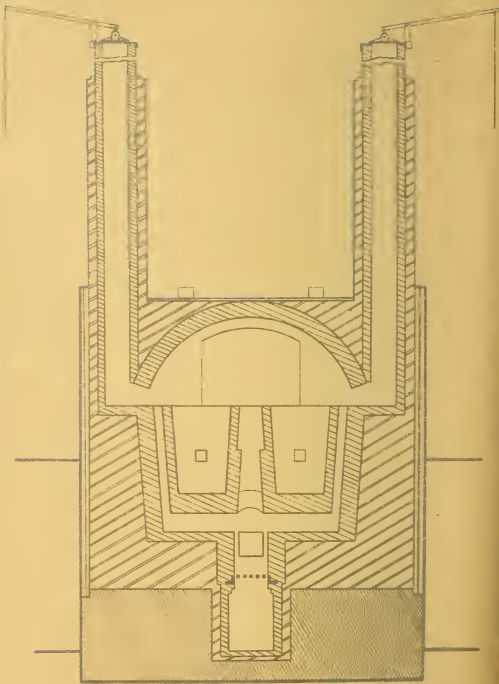
There are numerous modifications of the open hearth methods but the essential principles of the most important have been indicated above.

Cementation Process. Steel from Bar Iron; Hard or Tool Steel. The process of making steel from bar iron by carbonization is known as the cementation process. In this process bar iron imbedded in charcoal is subjected to the prolonged action of a high temperature. For this purpose bar iron of the best quality is cut into suitable lengths and placed in chests of fire-bricks. The chests are about ten or

twelve feet long, three to three and one-half feet wide and deep, and open at the top.

The charge of each chest generally consists of from six to eight tons of iron and two chests are inclosed in the same furnace. Ground charcoal is spread upon the bottom of the chests and upon this bars of iron are laid in regular order, small intervals being left between adjoining bars (the bars are about four inches wide and a little less than an inch thick). Charcoal is then added until the open spaces are filled and the bars covered by a continuous layer; over this another layer of bars is placed and the operations repeated until the chests are full. A thick layer of carbon is placed at the top and the whole is covered with a thick layer of grinders' waste (wheel-swarf, silica and iron dust from the grinder's wheel) or similar material. This substance at a moderate heat becomes plastic and forms a perfect cover to the chests and prevents contact of air with the charcoal. The chests are generally placed in pairs in a dome-shaped furnace, the fire-place being below the chests and the flues passing up between and at the sides, the whole being covered by a cone-shaped chimney fig. The temperature is raised gradually until it is about 2000° F., at which point it is maintained for a period of six or ten days, the time depending upon the quality of the steel required, the harder steel requiring the longer time. The progress of the operation is known by the appearance of trial bars, one of which is arranged in each chest so that it may be withdrawn when desired. When the operation is complete the bars are taken out and are found to have increased from one-half to one per cent in weight and are usually covered with hollow protuberances resembling blisters, hence the term "blister steel." Analysis shows that the increased weight is due to the combination of carbon with the iron and the carbon is found not only at the surface but also at the centre of the bars.

The chemistry of the process is believed to be due to the



action of carbon monoxide upon the iron. It has been shown experimentally that soft iron at a low red heat is capable of absorbing four times its volume of carbon monoxide, the action of the iron upon the gas is thought to be indicated by the reaction $\text{Fe}_x + 2\text{CO} = \text{Fe}_x\text{C} + \text{CO}_2$; the carbon dioxide produced is reconverted into carbon monoxide by the charcoal, $\text{CO}_2 + \text{C} = 2\text{CO}$. The carbon monoxide is produced in the first instance by the action of the small amount of atmospheric oxygen present in the chest upon the carbon. The carbon monoxide absorbed by heated iron is retained unchanged unless the temperature of the iron be raised above a red heat.

Shear Steel. Though carbon is found throughout the bars of the above described steel, it is more abundant nearer the surface, while below the surface are found numerous blister cavities. To render the steel more homogeneous and improve its quality much of it is subjected to a process of fagoting. The bars are broken, piled, heated, and forged into shape under the tilt-hammer as is the case with bar iron. One heating and welding constitutes single shear steel. The density, tenacity, malleability, and ductility of the steel are greatly increased by fagoting and such steel is suitable for the manufacture of certain kinds of tools, woolen shears being among them, hence the name shear steel. The fagoting operation repeated upon the single shear steel produces double shear, the latter again being superior to the single shear for certain purposes.

Crucible Steel; Cast Steel. The best steel for tools and for many other purposes is produced by melting blister steel in crucibles usually clay or plumbago.

The blister-bars are broken into fragments and a charge from fifty to one hundred pounds introduced into the crucible. The fusion is accomplished in a wind furnace, the surface of the metal being protected from oxidation by covering it with some fusible silicate or other flux. The fused contents of the

crucibles are poured into the moulds and when heavy ingots or castings have to be made the contents of several crucibles are poured into the same mould; sometimes this is done directly but generally in large castings the metal is poured from crucibles into a receiver and from that into the mould. The cast steel is more homogeneous than the shear steel and is used to make the finest cutlery.

Crucible steel is, apparently, justly thought better than that from other sources (Siemens and Bessemer). The cost of crucible steel limits its production to that of high quality for cutting instruments, for springs, for fire-arms, &c. Other material than blister bars is used for the production of crucible steel but even then the product is thought inferior to that from the former source. It is often found advantageous in crucible steel for special purposes to introduce some manganese. Small quantities of chromium, tungsten, silicon, nickel and titanium also appear to have beneficial effects upon steels desired for certain purposes.

Case-Hardening. Small objects which require the external hardness of steel can be made of bar iron and then hardened externally by heating them in contact with carbonaceous matter and afterwards cooling suddenly—this process is known as case-hardening. The reverse process to this consists in heating articles made of cast iron in contact with oxide of iron or other suitable oxidizing agent by which they are converted into malleable cast iron. In case-hardening carbonization is effected, in the reverse process decarburization.

Distinction between Steel, Cast and Bar Iron. Properties of Steel. These varieties of metal grade so imperceptibly into each other that it is impossible to classify them by any definition that will cover all the uses of the terms. The following distinctions are generally applicable—cast iron contains the greatest amount of carbon and is not malleable; steel is malleable and can be hardened by sudden cooling from high temperature; bar iron is malleable and can not be hardened by sudden cooling. Mild steel or ingot iron includes all the varieties of refined iron except the softest bar

iron and the hardest steel, that is all the refined iron made by the processes involving complete fusion (open hearth and Bessemer). Bar iron is pig-iron refined without complete fusion.

Steel is hardened by sudden cooling from a high temperature and it is usually done by plunging it into oil or water. It is tempered by reheating the previously hardened steel but not so highly as before, and cooling more or less suddenly. It is annealed by reheating the hardened steel and cooling slowly. After the first operation steel is hardest and most brittle, after the third it is softest and toughest, and after the second it is in an intermediate condition. The foregoing terms are not always used in the sense here given.

The mild steels have nearly entirely replaced bar iron in structural works. Steel has also displaced iron in armor plates in war vessels. The qualities of steel for this latter purpose have been greatly improved both by the foundry treatment of the large masses and by the addition of a small per cent of the other metals; the most important alloy being that with nickel, which is used in the celebrated Harvey process.

Chemical Properties of Iron. Pure iron is not acted upon by dry air at the common temperature. At a red heat it oxidizes and will burn at a white heat, in both cases forming the black oxide. The finely divided metal obtained by reducing the red oxide with hydrogen takes fire spontaneously when exposed to the air. At a red heat iron decomposes water with the liberation of hydrogen.

Pure water at the common temperature does not tarnish the surface of iron but the combined agency of water and carbon dioxide produces rusting which results from the formation of hydrated sesquioxide, $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$. In the action the carbonate is first produced and this is dissolved by the carbonic acid, the dissolved carbonate is decomposed by the oxygen of the air and converted into the hy-

hydrate ($\text{Fe} + \text{H}_2\text{O} + \text{CO}_2 = \text{FeCO}_3 + \text{H}_2$ and $4\text{FeCO}_3 + \text{O}_2 + 3\text{H}_2\text{O} = 2\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 4\text{CO}_2$) This reaction explains why the rusting of iron is so greatly facilitated by acid vapor. The stains so frequently observed to proceed from an iron nail are diffused by the formation and solution of the carbonate and subsequent conversion of it into the hydrate or other insoluble form; wet linen in contact with a nail is very soon thus stained.

Dilute sulphuric, nitric, and hydrochloric acids act readily upon iron but the two acids first named have no perceptible action when concentrated.

Iron forms two classes of compounds, the ferrous and ferric—in the first it is a dyad, in the second it may be regarded as a triad or tetrad.

Iron Oxides. There are three oxides of iron, FeO , Fe_2O_3 , and Fe_3O_4 .

Iron Monoxide; FeO . This is a powerful base and readily absorbs oxygen passing to Fe_2O_3 . It is not found in the free state but can be artificially produced by careful manipulation.

Sesquioxide of Iron; Ferric Oxide; Red Oxide; Fe_2O_3 . This oxide is a weak base and is isomorphous with alumina. It occurs abundantly in nature as specular iron ore of which there are many varieties. The artificial sesquioxide is frequently used as a red pigment under the name of Venetian red. For this purpose it is prepared by decomposing the ferrous sulphate by heat. The hydrated sesquioxide constitutes the brown hæmatite or limonite ore.

The sesquioxide and its hydrate are the common coloring matter of the soils. Its presence in the soils favors the decomposition of organic matters by supplying oxygen to them. In this action the ferric oxide is reduced to the ferrous, this latter then combines with the oxygen of the air and reforms the ferric oxide. This operation is continually repeated, the ferrous oxide acting as a carrier of oxygen from the air to the decomposing body. When the ferric

oxide is heated to whiteness or in a reducing flame it loses oxygen and passes to the tetroxide.

Triferrie Tetroxide; Magnetic Oxide; Black Oxide; Fe_3O_4 .

This oxide occurs abundantly in nature and is one of the chief ores of iron. It is always produced when iron is oxidized at a high temperature. It is a very stable compound which fact has led to its use as a covering to protect against rust. In the Bower-Barff process the metal heated to redness is subjected to the action of steam by which it receives a dense film of the oxide. The same result is obtained by subjecting the heated metal to the action of the carbon di monoxide and air.

Iron Carbonate; Spathic Ore; Siderite; $FeCO_3$. The carbonate occurs abundantly in nature and is a valuable ore of iron. It is often associated with the carbonates of calcium, magnesium, and manganese, with which it is isomorphous. It is often found in natural waters, being soluble in water containing carbon dioxide. Mineral springs containing the carbonate in solution are called chalybeate springs. For reasons already explained these waters usually deposit the hydrated oxide when exposed to the air, hence the rusty deposit which always occurs about such springs.

Ferric Sulphide; Iron Pyrites; FeS_2 . This is the most important sulphide and occurs widely and abundantly in nature. It is sometimes used as an ore of iron but more generally as an ore of sulphur. It is generally known under the name of pyrite or iron pyrites. There are two other sulphides of iron, FeS and Fe_3S_4 . The first is used in the laboratory for making hydrogen sulphide and is itself prepared by heating iron filings and sulphur together. The Fe_3S_4 occurs in nature under the name of magnetic pyrites.

Ferrous Sulphate; Copperas; Green Vitriol; $FeSO_4$, Aq. Ferrous sulphate is obtained in large quantity as a bye-product in the manufacture of alum. It is made directly in large quantity by dissolving scrap iron in warm sulphuric acid, evaporating and crystallizing. It is also made by oxi-

dizing the burnt pyrites left in the manufacture of sulphuric acid.

The salt crystallizes in green crystals which are usually tinged with a yellowish white, due to the presence of ferric sulphate. Ferrous sulphate is largely used in dyeing, tanning, and in the manufacture of inks, Prussian blue, Venetian red, and other pigments. It is a great oxidizing agent and because of this power it is used to precipitate gold from solution and will reduce indigo to the soluble condition.

There is a number of other sulphates of iron the most important of which is the ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$. It has been found in nature and can be produced artificially. Solutions of this salt mixed with solutions of potassium and ammonium sulphates produce iron alums.

Other Compounds of Iron. Iron forms two chlorides, ferrous and ferric; the solution of the first is used medicinally and that of the second for disinfecting. It forms two iodides corresponding to the chlorides. It also forms ferrous and ferric phosphates and nitrates and a number of other inorganic compounds too numerous and unimportant to be considered here.

Reactions of Iron Salts. *Ferrous Salts.* By the addition of caustic alkaline solutions or ammonia, ferrous salts give white precipitates, rapidly changing to green and brown. Carbonates of potassium, sodium, and ammonium give white precipitates which change to yellowish brown. Hydrogen sulphide gives no precipitate. Ammonium sulphide $(\text{NH}_4)_2\text{S}$ precipitates black iron sulphide soluble in acids. Potassium ferri-cyanide gives a deep blue precipitate.

Ferric Salts. These give Prussian blue precipitate with potassium ferrocyanide and intense blue-black with infusion of nut-galls (gallo-tannic acid).

COBALT.

Cobalt occurs in nature often associated with nickel. Its chief ores are the arsenide and sulphide. Cobalt is magnetic like iron and closely resembles iron in other properties. The metal has found no application except to a small extent in plating, as with nickel. This is accomplished by the electrolysis of a solution of the double sulphate of

cobalt and ammonium. The deposit is harder, more tenacious, and of greater beauty than nickel. It has been termed superior nickel plating.

Useful Compounds of Cobalt. Several cobalt compounds are of considerable importance in the arts being used to produce permanent and brilliant colors. Some of the most important of these are smalt, Thénard's blue or ultramarine.

Smalt. Smalt is a blue pigment very extensively used in the arts. It is a potash glass colored with the oxide of cobalt and consists of a mixture of the silicates of potassium and cobalt and sometimes other metals. It is used in painting on porcelain, in making stained window glass, in making tiles, and as a blue pigment.

Thénard's Blue; Cobalt Ultramarine. This pigment consists of alumina colored with the oxide or phosphate of cobalt. It is used both as a water and an oil color. There is a number of other permanent pigments prepared from the compounds of cobalt.

Cobalt Chloride. This salt is a basis of one of the sympathetic inks. A dilute solution of the chloride has a faint rose color which is not visible on paper but turns blue upon drying, due to loss of water of crystallization; it disappears again upon cooling due to absorption of atmospheric moisture.

NICKEL.

Nickel resembles iron and cobalt in many of its properties. It is malleable and ductile and next to manganese it is the hardest of the metals. It is magnetic, like iron and cobalt and occurs nearly always in meteoric iron. The ores of nickel are found in numerous places throughout the world but are generally very complex, usually being associated with a number of other metals.

Nickel is largely used for coating iron and other bodies by electrolysis, a solution of the sulphate being used for the purpose. It is made into crucibles and dishes, for use in the laboratory. It is used for coin and for making various alloys. Alloyed with copper and zinc it forms German silver. The alloy of nickel with steel very greatly excels the steel in the important qualities required in armor plates. Processes have been devised for rolling nickel into thin sheets, and these can be welded to iron and steel plates. Pure nickel resists the action of the atmosphere and both fresh and salt water almost as well as the precious metals.

MANGANESE.

Manganese is not used in the metallic state. It resembles iron in many of its properties and its ores are often found associated with those of iron. It occurs in nature in many forms but its principal ore is Pyrolusite, MnO_2 .

Pyrolusite; MnO_2 . This oxide is largely used in the preparation of chlorine and oxygen and in the manufacture of glass; it is also the source of the other compounds of manganese.

Other Oxides of Manganese. The higher oxides of manganese are acidic; Mn_2O_3 and Mn_2O_7 . The latter in contact with water produces permanganic acid, $\text{H}_2\text{Mn}_2\text{O}_8$. This acid and its alkaline salts are powerful oxidizing agents. By virtue of this property potassium permanganate finds application in the laboratory and is used as a disinfectant, Condy's disinfecting fluid being composed of it. The sodium permanganate generally displaces it as a disinfectant it being the cheaper.

Ferro-Manganese; Spiegeleisen. These bodies are alloys of iron and manganese rich in carbon. The first is the richer in manganese. Both Spiegeleisen and ferro-manganese are largely used in the manufacture of Bessemer and Open Hearth steel.

CHROMIUM.

Chromium in the metallic state finds no useful application. Some of its compounds are largely used in the preparation of pigments. It derives its name from the Greek word *χρῶμα* because of the color of its compounds. Chromium is generally found in nature as an oxide in combination with iron oxide. Its alloys with iron are important. The presence of chromium in iron or steel increases the tenacity, hardness, and elasticity and gives finer texture.

Important Compounds of Chromium. The compounds of chromium most used in the arts are chromates, compounds in which the chromium oxide takes the part of an acid radical. These chromates are all made directly by the oxidation of the chrome iron ore (FeO , Cr_2O_3).

Potassium chromate and bichromate are thus made, the latter $\text{K}_2\text{Cr}_2\text{O}_7$ in large quantities, and other compounds of chromium are derived from them.

Potassium bichromate is used in the preparation of nearly all chrome pigments, and in the production of a variety of colors in dyeing and calico printing. It is a powerful oxidizing agent and is used in the manufacture of safety matches and as a source of oxygen for organic analysis. It is readily reduced by organic matter and is an agent frequently employed in testing the purity of water. Mixed with gelatine and exposed to the light it is reduced and the gelatine rendered

insoluble. This fact is taken advantage of in photography and is the basis of the carbon process.

Lead Chromate; Chrome Yellow, and Orange Chrome. The lead chromate constitutes two of the most important chrome colors, chrome yellow and orange chrome. Chrome yellow is the normal chromate of lead (PbCrO_4), and is prepared by bringing together in solution lead acetate and potassium chromate. It is largely used in painting and in calico printing. Orange chrome is the basic chromate of lead (PbCrO_4 , PbO) and may be obtained by boiling the normal chromate with lime by which a portion of the acid is removed. Stuffs made yellow with the normal chromate may be made orange by a bath of lime water.

There are many other chrome colors which are of great permanence and have many applications.

MOLYBDENUM, TUNGSTEN, AND URANIUM.

The metals molybdenum, tungsten, and uranium are not used in the metallic state. Their compounds have been but little studied and are not of great importance.

Like chromium they all form acid oxides.

The compounds of molybdenum find no useful application in the arts, but some of them are useful as special reagents in the laboratory.

Tungsten alloyed with steel in certain proportions improves its properties in several respects and such alloy is used in the preparation of certain tools. Sodium tungstate is used as a mordant and muslin steeped in a solution of this salt will not burn with a flame. Some of the tungstates are used to a certain extent in the preparation of pigments. The tungstate of calcium has found recent application in forming a fluorescent surface for detecting the Roentgen rays.

The oxides of uranium are valuable for glazing porcelain black and sodium uranite is prized for painting and staining glass under the name of uranium yellow.

BISMUTH AND ANTIMONY.

Bismuth. This metal is found native in small quantities in widely distributed localities. In the metallic state it is used only for the construction of the electric thermo-pile, being too brittle for other use. Bismuth is chiefly used in the preparation of alloys. It usually confers hardness and fusibility upon the alloys and causes them to expand in solidifying.

Fusible metal is an alloy of two parts of bismuth, one of tin, and one of lead. This alloy fuses below 180°C . though the fusing point of tin, the most fusible of the three, is much above this. An alloy of three parts of lead and two of bismuth has ten times the hardness and twenty times the tenacity of lead. An alloy of lead, tin, and bismuth

is largely used for the electrotyping process, it is very fusible and takes a fine impression of the mould.

Compounds of Bismuth. The oxide of bismuth (Bi_2O_3) is used to a limited extent for glass and porcelain staining. Bismuth nitrate is largely used medicinally and also as a colorless flux for certain enamels. The oxychloride of bismuth is used to a limited extent as a pigment under the name of pearl white.

Antimony. Antimony like bismuth is too brittle for use in the metallic state. Its only application as a metal is the construction of thermo-piles in conjunction with bismuth. Antimony forms valuable alloys. It generally increases the fusibility, hardness, and brittleness of the metals and confers the property of expanding upon solidification. It is accordingly one of the constituents of type-metal, lead being the other. The same metals with tin are used for stereotype plates. With nine-tenths tin it forms Britannia metal. The number of useful alloys of this metal is large.

Important Compounds of Antimony. Antimony sulphide, Sb_2S_3 . This sulphide is used in the preparation of safety matches and is frequently one of the constituents of the friction tube composition used in firing cannon. It gives a bluish white flame with nitre and is used in pyrotechny. This sulphide roasted in air and largely converted into the oxide is used for coloring glass yellow. The antimony penta-sulphide (Sb_2S_5) is used for vulcanizing rubber. The sulphides of antimony are used as a basis for the production of a number of pigments.

TANTALUM, NIOBIUM, AND VANADIUM.

These elements are only obtained in the metallic state with difficulty. Neither the first two nor any of their compounds have been put to any useful application. Vanadium is widely distributed but occurs in small quantities. Some of the vanadic compounds are used in the preparation of pigments, of aniline black, and for dyeing leather black.

TIN; Sn.

Tin is a metal of great antiquity. It is mentioned in the Bible and was one of the common metals in the time of Moses. Numerous bronze implements containing tin have been found in the ruins of Nineveh. It is probable but not certain that the Phœnicians obtained the tin ore from what are now Cornwall and Devon, more than 1000 years B. C. Some of the early bronzes contained tin and agree closely in composition with statuary bronze of the present time. The Romans used the metal for tinning the interior of copper vessels just as is done to-day.

Occurrence and Preparation. Tin has not been found native. It occurs in combination as a sulphide and as an oxide. The latter SnO_2 is the ore from which nearly all the metal is obtained. The islands of Banca, Malacca, and the British Isles produce the greater portion of the tin.

Tin Reduction. For reduction the best quality of tin ore is crushed and washed to remove as much of the gangue as possible. The ore is then mixed with coal and heated, usually in a reverberatory furnace, the air being excluded to favor the reducing action of the carbon. If the ore is refractory some flux is added to form a slag. The metal thus obtained is fused and cast into blocks which are fused again and the tin refined thus giving several grades of quality.

Properties of Tin. Pure tin is nearly the color of silver. It is soft and malleable at ordinary temperatures and emits a crackling sound when bent or twisted. It is the most fusible of the common metals (227°C.). It is intermediate in hardness between lead and zinc. Its specific gravity is 7.3. Its malleability increases up to 100°C. ; at this point its malleability is only exceeded by gold, silver, and copper. Heated near to its ^{melting} boiling point it becomes brittle. It has little tenacity. It is little affected by air and moisture at common temperatures, but if kept fused in contact with the air it oxidizes rapidly forming a white powder. It is readily soluble in hydrochloric acid with evolution of hydrogen and dilute nitric acid acts upon it with great energy converting it into a white powder.

According to Bloxam extreme cold converts tin into a modification known as *grey tin*. The specific gravity of grey tin is only 5.73 and when fused it becomes ordinary tin. Spontaneous disintegration may occur from great reduction of temperature.

Uses of Tin. Tinning. Owing to its permanence under ordinary influences and its resistance to vegetable acids, tin is largely used for coating other metals. The manufacture of tin-plate absorbs more tin than any other industry. Tin-plate

(or the material of which ordinary articles consist, called tin) is made by coating iron or very mild steel with tin. Steel which is now most generally used is first carefully annealed. The annealed steel or iron plates are first carefully cleaned so as to present a chemically clean surface. The cleaned plates are then dipped once or twice into melted tin. The tin coating protects the iron or steel plate so long as the surface is unbroken, but when the iron is exposed the two metals form an electric pair and the iron is most readily attacked and eaten away. With a zinc coating under similar circumstances the zinc is attacked.

Tin-plate is made in large quantities in Europe and the industry is now being introduced into this country. Tin is also used to coat the interior of lead or other pipes used by brewers, distillers, and others.

Interne plate the coating is an alloy of tin and lead.

Culinary utensils are frequently tinned inside. This process is simple and has been practiced for many centuries. The surface of the utensil to be tinned which may be copper, brass, or iron, is made chemically clean. Some tin melted in the vessel is then spread over the surface with tow. A skillful workman thus produces a thin uniform layer of tin, which greatly increases the wearing power of the vessel and almost imperceptibly adds to the weight. So slight is the increase of weight that the Ancients thought that there was none and Pliny expresses surprise at so remarkable a result.

Alloys. Tin enters into the composition of a large number of alloys. It alloys with lead in all proportions and many solders and pewters are composed of these metals, all of which melt at temperatures lower than does either constituent. In applying a solder the surfaces to be joined should be chemically clean and borax or sal-ammoniac is generally applied to dissolve off any oxide.

Gun metal and bronze are alloys of copper and tin.

Oxides and Salts of Tin. Besides the binoxide of tin (SnO_2) there is a monoxide (SnO). Each of these oxides forms a series of salts, the first acting as an acid and the second as a basic oxide. There have been obtained several other oxides. The stannic oxide by hydration forms two important acids the stannic and meta-stannic. These acids form a large number of salts the most important of which is the sodium stannate, largely used as a mordant in dyeing and calico printing.

Tin forms two classes of salts (stannic and stannous) corresponding to both hydracids and oxyacids. None of these salts are of great technical importance though some of them are used in dyeing and calico printing. Several tin salts of vegetable acids (oxalate, acetate, citrate, and tartrate) are similarly used.

TITANIUM, ZIRCONIUM, THORIUM, GERMANIUM, AND CERIUM.

These four metals are among the rare elements and have found no useful applications. Titanium is remarkable in that it combines directly with nitrogen when strongly heated in air. Titanic acid has been employed in the manufacture of artificial teeth. The oxide of thorium together with those of cerium and zirconium is used in the preparation of the mantle of the Wellsbach burners. The other compounds of these metals are not of technical importance and can not be described here.

LEAD; Pb''; 207.

Occurrence. It is doubtful whether lead has ever been found in the native state, but it occurs in a large number of natural compounds. Only a few of these compounds can be classed as ores of lead. The sulphide or galena, PbS , is the most abundant and principal ore of lead. The carbonate and sulphate are met with in certain localities in sufficient quantity to form important ores. The compounds of lead with oxygen, sulphur, and arsenic are also frequently sources of lead, especially in the working of such compounds for the silver contained.

METALLURGY OF LEAD.

Until about 1870 substantially all the lead in commerce was obtained from galena or galenite, PbS . This ore is still the source of nearly all the lead, but the metal itself is now obtained in enormous quantity as a bye-product in the reduction of silver. In these cases in addition to the lead sul-

phide there are often present several other compounds of lead, mainly those above mentioned. Lead is obtained in silver and gold mining in such large quantities that the method of producing the enriched lead or "base bullion," as it is called, might with equal propriety be described along with those metals.

The method of obtaining the lead from the galena is simple in principle and execution when the ore is comparatively pure, but with impure ore the processes increase in complexity and number. The processes may be conveniently separated into three: *1st. The method of self-reduction; 2nd. The method of roasting, oxidation, and subsequent reduction by carbon; 3rd. Reduction by iron.*

First Process. The simplest method of reduction is carried out in a reverberatory furnace and is usually termed the *air reduction* or *self-reduction* method. In this method the galena is roasted at a moderate heat and partially converted into the oxide and sulphate. The temperature is then raised and the unchanged sulphide reacts upon the oxide and sulphate, freeing the lead, $2\text{PbO} + \text{PbS} = \text{SO}_2 + 3\text{Pb}$ and $\text{PbS} + \text{PbSO}_4 = 2\text{Pb} + 2\text{SO}_2$. A small quantity of lime is usually added with the ore for the purpose of forming a slag with the siliceous matter present. This method is applicable to the purer forms of galena. The other two methods to be mentioned are applicable to ores poorer in lead or associated with other minerals which make their reduction in reverberatory furnaces impracticable.

Second Process. The second method consists in converting the galena into oxide and reducing the oxide with carbonaceous matter.

In this method the ore is first roasted until free or very nearly free from sulphur. It is then mixed with fuel and flux (iron oxide and lime) and smelted in a blast furnace. The lead is reduced by the carbonaceous matter and the impurities are removed as slag. The first heating in the process is generally accomplished in a calciner (a kind of reverberatory furnace).

The Third Process. In this process the raw ores are treated direct in a blast furnace and the reducing agent is iron, $\text{PbS} + \text{Fe} = \text{Pb} + \text{FeS}$. In this method the ore is treated in a blast furnace and there is added to the charge, if iron oxide is not already present in the ore, metallic iron or more generally rich iron slags or iron ore. In the latter cases the iron ores are reduced by the carbonaceous matter of the fuel and the melted iron decomposes the galena, freeing the lead and forming iron sulphide as indicated above.

The iron sulphide formed combines with some of the lead sulphide and other sulphides present in the ore and yields a matte which is lighter than the lead and easily separated from it. The matte is subjected to other treatment for saving the lead, copper, and silver when the latter are present. The slags of the first and second processes are often treated by the third method. Some lead ores are treated by two of the above processes. Galena has also been reduced by iron directly in a reverberatory furnace.

American Western Method. The last two processes have been substantially combined in one in this country and it has been used extensively for the production of enormous quantities of argentiferous lead, notably at Leadville, Colorado, and Eureka, Nevada. The modified process consists in treating the raw ore direct in blast furnaces. If the gangue does not contain the necessary ingredients the ore is mixed with the proper material for flux and charged into the furnace with carbonaceous fuel. The charge of the furnace in general terms consists of the ore and gangue to which, depending upon their composition, is added one or more fluxes, as iron ore, siliceous matter, and limestone or dolomite. The result of the smelting operation gives three distinct products, all of which are drawn from the same furnace in the liquid state. The lowest is the rich lead called "base-bullion," which is drawn off into pigs, preparatory to refining. The second is termed "speiss" and is principally composed of a combination of iron with arsenic and sulphur; antimony and other metals are often present in small quan-

tity. The third layer is the slag and consists essentially of the silicate of iron.

The "speiss" is frequently divisible into two parts, the "speiss" proper and the matte; the matte is mainly iron sulphide, the "speiss" proper is iron combined with arsenic and antimony. The matte carries more silver than the "speiss" proper and is sometimes worked over. The "speiss" carries more gold than the matte and some silver, but no way of extracting the gold economically has been invented. This "speiss" has been produced in great quantities at the western smelting works and contains a large amount of gold and silver.

In the smelting of lead ores considerable quantities of lead fume are carried off with the smoke from the furnaces and many processes have been tried for the collection and saving of this lead. The method usually adopted is to cause the furnace gases to pass through a series of flues aggregating several miles in length. The lead fume settles very slowly even in quiescent air, which fact explains the great length of the flues. These flues are cleared out at intervals and much fume secured. The fume consists of lead sulphate, lead oxide, and lead sulphide.

DESILVERIZING LEAD.

When lead from any of the above sources contains enough silver to make its extraction profitable it is desilverized. The production of the lead at many of the western works is but the first step toward obtaining the accompanying silver and such lead is always desilverized. The silver can be extracted with profit when the lead contains one ounce of silver to the ton.

The desilverizing process involves three distinct operations—"softening," concentration, and cupellation. The object of the first is to remove base metals which would interfere with the separation of the silver and lead; the second is to concentrate the silver in a smaller quantity of the lead; the

third is to complete the separation of the silver from the remaining portion of the lead.

The preliminary operation to the concentration is "softening" the lead, sometimes in our western states merely termed "calcining." The object of "softening" is to remove from the lead antimony, copper, or other oxidizable metals as fully as possible. This removal is accomplished by taking advantage of the difference of fusibility and difference of oxidizability. The "softening" is effected in a reverberatory furnace. The smelted lead is fused at a low temperature and the copper being the less fusible can be partially removed as a scum from the lead, which fuses first. The heated air plays upon the molten metal by which the more oxidizable bodies are converted into oxides which float upon the surface and are removed. This continually exposes fresh surfaces of the metal to the action of the air and facilitates the oxidation of the impurities. When the impurities are too abundant for this ordinary treatment, the melted metal is agitated by a jet of steam discharged into it which is more efficient in exposing the metal to the action of the air. In this operation some of the lead is of course oxidized and carried off with the other impurities, but these oxidized products are all worked over again to recover the metals contained. These products from the "softening" furnace are called "crasses," the term slag having very appropriately been limited to fusible silicate.

Parke's Desilverizing Process. After "softening" the further concentration of the silver in the lead or the desilverization of the "base-bullion" in this country, is accomplished by Parke's desilverizing process. This process depends upon the fact that zinc alloys more readily with silver than with lead, and when zinc is melted with argentiferous lead and the mixture allowed to cool, the portion which first solidifies is an alloy of silver, zinc, and lead containing nearly all the

silver and only a small amount of lead. The zinc employed amounts to about two per cent of the lead treated.

From the rich alloy of zinc, lead, and silver, the zinc is separated by distillation and used again. The remaining alloy of lead and silver is subjected to cupellation which separates the silver from the lead. The cupellation will be described after we have explained the principles of another important process for concentration.

Pattinson's Desilverizing Process. This process depends upon the fact that an alloy of lead and silver is more fusible than the lead itself. In Pattinson's process the argentiferous lead is melted and allowed to cool slowly while being constantly stirred. Near the melting temperature of the lead this metal crystallizes out carrying only very minute quantities of silver—these crystals are continually removed and the lead left behind is very rich in silver.

A modification of the Pattinson process consists in agitation of the molten metal by a jet of high pressure steam—this facilitates the crystallization of the lead and removes more fully copper and antimony; it also saves time and labor. In this method the enriched alloy is drawn off in the liquid state from the lead. This modified process is known as that of Rozan. It was long employed at the Richmond mines at Eureka, Nevada, and is not used elsewhere in this country.

Cupellation. The rich lead obtained by either of the processes just described is then subjected to cupellation or refining. This operation depends upon the fact that the melted lead readily oxidizes in air while silver does not. The fine lead is melted in a cupel on the hearth of a reverberatory furnace. The cupels are about four or five feet long and two or three feet wide and six or seven inches deep. They are made of bone ash and pearl ash. Over the melted surface of the lead a blast of air is made to play. The lead is rapidly oxidized and the blast drives the oxide to the mouth of

the refinery where it flows out in the liquid state into pots and is removed. As the oxidation proceeds more lead is added and the operation is not generally completed in a single cupel. When the silver amounts to about one-tenth of the contents the concentrate is drawn off and the oxidation completed in a second cupel. The oxide of lead which is removed carries some silver and is always reduced again. The bottoms of the cupels become saturated with lead oxide and are broken up and smelted in the blast furnace.

Properties of Lead. Lead is a bluish grey metal. It is so soft as to leave a streak when rubbed on paper. It is malleable and ductile but has little tenacity. Its hardness is increased by zinc, antimony, and copper. Its specific gravity varies with the conditions under which it is obtained but is about 11.3. Its fusing point is 235° C. It is readily oxidized in the presence of moist air and then in the presence of acid vapors forms salts. The basic carbonate of lead thus often results from the action of the carbon dioxide of the air. In a finely divided state lead is pyrophoric.

The action of water upon lead is influenced by the salts dissolved in the water. Nitrites and nitrates increase the action of water upon lead and the sulphates and carbonates decrease this action. The fact that lead is a cumulative poison and that water long in contact with it is liable to contain some lead, make great care necessary in using waters that have been in contact with lead. Water that has been standing long in lead pipes or conveyed for long distances in such pipes should not be habitually used for drinking.

Dilute nitric acid acts readily upon lead but it resists the action of all the other common mineral acids when at the common temperature—even hydrofluoric acid does not attack it. Hot concentrated hydrochloric and sulphuric acids act upon it.

Uses of Lead. Lead is largely used in the form of sheets, water channels, pipes and in construction work. Its resist-

ance to the action of acids makes it very useful in sulphuric acid works and in many appliances of the chemical laboratory. It finds many uses in the preparation of alloys, type metal, pewter, solder, &c.

It is the metal from which shot are made and for this purpose the molten metal is caused to flow through ^wcollenders of proper size and to fall for some distance through the air into vessels holding water. A small amount of arsenic (two per cent) is always alloyed with the lead in this operation. The arsenic makes the lead more fluid, hardens it when cool, and increases its tendency to take the spherical form in passing through the air. The size of the holes in the collender, which must be smooth and round, the temperature of the melted lead, and the distance through which it falls determine the size of the shot. The length of the tower varies from thirty feet for small to fifty feet for large shot.

Lead pipes are usually made by forcing the melted metal through the annular space between a die and a concentric spindle or mandril, the die fixing the exterior diameter of the pipe and the mandril the interior. The largest amount of lead is consumed in the manufacture of white lead.

Lead Oxides. There are five oxides of lead known, the most important of which are the monoxide and red lead (PbO and Pb_3O_4).

Lead Monoxide; PbO . This body occasionally occurs native. There are two varieties of the artificial product massicot and litharge. Massicot is produced when melted lead is heated at a ~~common~~ moderate temperature in the air and it is a yellow powder. When the oxidation takes place at a temperature sufficiently high to fuse the oxide formed, it gives litharge, which is reddish brown in color. Litharge readily combines with silica at high temperature and forms lead silicate. It is largely used in the manufacture of flint glass and in glazing earthen ware; it is also used for the production of lead acetate and other lead salts.

Red Lead; Minium; Pb_3O_4 . Red lead is made by heating massicot in air at a temperature not high enough to fuse it. It is largely used in the manufacture of flint glass, as a cement in steam joints, as an oxidizing agent in the manufacture of matches, and as a pigment.

White Lead; Basic Lead Carbonate. The commercial white lead is essentially a basic carbonate, which results from the combination of the normal carbonate with one or more molecules of lead hydrate, $2PbCO_3, Pb(OH)_2$. Many methods have been invented and tried for the manufacture of this important compound. All of these which have been commercially successful depend upon the same principle, the formation of a basic salt of lead and the decomposition of this salt by carbon dioxide. The oldest method (the Dutch method) and that which still gives the best white lead for paints depends upon the formation of a basic acetate of lead and the conversion of this into white lead by carbon dioxide. In this method thin sheets of metallic lead are exposed to the combined action of the vapor of acetic acid and carbon dioxide. The lead is gradually converted into white lead, which has to be separated from the metallic lead, ground, and washed. The chemical actions which produce the result are, first, the production of a normal lead acetate which combines with the lead hydrate to form basic lead acetate. Then the carbon dioxide decomposes the basic acetate forming basic carbonate and reproducing the normal acetate. This action is then repeated so that the acetic acid acts as a carrier between the lead and the carbon dioxide. A small amount of the acetic acid will convert a large amount of lead into the carbonate. The above method is also used in England.

White lead by this method has retained its superiority over all others as a pigment. This superiority consists in greater covering power, durability, and opacity. These properties are believed to be due to the fact that the Dutch

pigment in its ultimate constitution is less crystalline and more nearly amorphous than that from any other source.

Various efforts have been made to hasten the process for the production of white lead among which are the German and French methods. In the former the actions described are aided by artificial heat the reagents being enclosed in stoves. The French method (Clichy) involves the separate preparation of lead oxide and the action of acetic acid upon it, the result being treated with carbon dioxide. This method slightly modified is largely used in this country. Another process (Milner's) consists in the production of a basic chloride of lead by the action of litharge, common salt, and water upon each other and the subsequent precipitation of the chloride with carbon dioxide. The above processes are all that have succeeded commercially and while the newer processes are cheaper than the Dutch the product is not as valuable as a pigment.

A new American method has just been announced by which the pigment is prepared by electrolysis. Sodium nitrate is decomposed by the electric current between lead and copper electrodes. Lead nitrate and sodium hydroxide are thus formed and dissolved at the two electrodes. The solutions are drawn off and mixed in the proper proportions when sodium nitrate is reproduced and lead hydrate precipitated as an amorphous powder. This nitrate may be again electrolysed. A solution of sodium carbonate is added to the lead hydrate by which sodium hydroxide and basic lead carbonate are formed. The hydroxide of sodium can again be converted into the carbonate by carbon dioxide and used again. The sodium nitrate and carbonate being repeatedly used are only consumed in small quantities. The advantages of this process are that no free acids are used, that the operation is complete in a day, and that the process is non-poisoning—the pigment being produced in the form of powder and no grinding being necessary. It is claimed that the product is more amorphous than the Dutch pigment and consequently superior to it.

Properties and Uses of White Lead. The pigment is a heavy white powder. It is poisonous and the separation and grinding of the product in the English-Dutch method often leads to lead poisoning among the operatives. The difficulty of avoiding these effects constitutes a grave objection to the process.

The principal use of white lead is for painting. It is thought that when white lead is mixed with oil it saponifies some of the oil and that to this fact is partly due its superi-

ority as a pigment. Lead paints are discolored by hydrogen sulphide from the formation of lead sulphide. Painting which has been blackened thus may often be restored by exposure to light and air by which the sulphide is oxidized to the sulphate. White lead is sometimes adulterated with barium sulphate and certain pigments are made by mixing the two in certain proportions. It has been proposed to use lead sulphate as a substitute for white lead but none of these products give as good results as the pure pigment.

Other Compounds of Lead. In addition to the compounds of lead already referred to there is a number of others, none of which are of any commercial importance nor of special use in the laboratory. Some of the oxychlorides are used to a limited extent as pigments—Pattinson's oxychloride gives a white pigment and Paris yellow and Turner's yellow belong to this class of bodies.

COPPER; Cu; 63.2.

Occurrence. Copper occurs abundantly in the native state and as a constituent in many natural compounds. Among these compounds the principal ores of copper are the oxides, carbonates, and various sulphuretted forms. These last constitute the most abundant ores of copper and the most important of them is the copper pyrites, a double sulphide of copper and iron (Cu_2S , Fe_2S_3) though there are several other sulphides of copper.

These ores of copper in addition to the gangue are very frequently associated with the sulphides and arsenides of other metals as iron, antimony, lead, zinc, and silver; gold is also often present.

Copper Reduction. Copper is obtained from its ores by two processes usually termed the *wet* and *dry*, the latter involving fusion and the former not. The method involving fusion is the more important industrially. The object of the reduction is of course in all cases to separate the copper from the impurities present.

In the United States the great bulk of the copper is

obtained from three localities, the region of Lake Superior, from Montana, and from Arizona. In the Lake Superior region the copper is mainly in the native form, in Montana the sulphuretted compounds exist, and in Arizona the oxidized forms abound together with the sulphides. The dry method or the method of fusion is employed in all these localities.

Dry Reduction. 1, Concentration of Native Copper; Lake Superior. Although there have been found immense masses of native copper in these mines varying from forty to four hundred tons, these large masses have not been the principal sources of the metal. The bulk of the copper of these mines is distributed in fine grains through the gangue stone, which is either amygdaloid or conglomerate rock. The rock is crushed by steam stamps in the mill and the metal is separated from the gangue by washing. The crushed metal ^{is} in its descent over a series of cradles which are continually "jigged" or given a jerky motion, is subjected to the action of running water. By this means the metal which is heavier collects below the sand, the larger grains nearer the stamps, the moveable earthy matter being carried along by the water. At the lower end of the incline the finer sediment is subjected to special treatment on sluice-tables or "buddlers" to collect the very finely divided copper.

The gangue remaining with the copper is separated by fusion with a little flux in a reverberatory furnace and copper of great purity obtained. The ores from which the copper is obtained vary in richness from .6 to 3 per cent of metal. The method of obtaining the copper from the ore at Lake Superior is so simple that it is usually termed mechanical concentration, but since the product is fused and refined it is here included under dry reduction.

Dry Reduction. 2, Reduction of Oxidized Copper Ores. In the Arizona mines a large part of the ores worked ^{up to} at the present time have been oxidized forms. These are reduced

in blast furnaces, coke being generally the fuel employed. The purity of the oxidized ores (oxides and carbonates) frequently permits the production of a high grade of copper by the single operation of smelting in the blast furnace with carbonaceous matter as reducing agent. The Arizona copper ranks next to the Lake Superior in purity. In these mines the proportion of the oxidized ores decreases and of the sulphuretted ores increases as the depth increases. The reduction of the sulphides depends upon the principles to be described.

Dry Reduction. 3, Reduction of Copper Sulphides. The sulphuretted ores of copper are those most largely employed throughout the world for obtaining the metal. These ores are extensively worked in the Western mines in this country. The sulphuretted ores are becoming more and more important at the Arizona mines and considerable copper now comes from the copper bearing silver and lead ores of Colorado.

In the reduction of the sulphides use is made of the principle that copper sulphide is less easily reduced than the other metallic sulphides present in the ore, of these iron is the most important.

The older process of reduction consists of a series of roastings (heating in air) and fusions of the ore, the number of operations varying with the nature and quality of the ore. The object of the roasting is to expel arsenic, some of the sulphur and antimony, and to oxidize the iron. After the first roasting the ore is fused with the proper flux to form a slag with the gangue and iron oxide. In this operation the gangue and some of the iron are removed and coarse metal or a "matte" is obtained. The "matte" is essentially a double sulphide of copper and iron with greatly reduced quantities of antimony and arsenic. This "matte" is then broken up and the operation of roasting and fusion is again repeated by which "white" metal is obtained; this is copper sulphide nearly free from

iron and other base metals. The "white" metal has to be again fused in an oxidizing atmosphere by which self-reduction takes place, $\text{Cu}_2\text{S} + 2\text{CuO} = \text{Cu}_4 + \text{SO}_2$, and "blister" copper is obtained; or the oxidizing action may be continued until all the sulphur is expelled and the copper oxide formed reduced by carbonaceous matter. The "blister" copper has then to be refined to remove any remaining sulphur and the small quantities of the baser metals still left. During all the operations sulphur, arsenic, and antimony are gradually eliminated. The roasting of the ores and "matte" may be accomplished in heaps, or stalls (which are rectangular open brick enclosures) reverberatory furnaces, or roasting cylinders. The fusion of the roasted products is accomplished in reverberatory furnaces or shaft furnaces.

It will be observed that the above method consists of a series of roastings in which the oxidizable impurities are oxidized together with some of the copper. These are followed by smelting operations by which the copper is deoxidized by some of the remaining sulphur and the iron removed as a slag. It would be impracticable to here describe in detail all the steps in the smelting of sulphuretted ores. The charges of one operation are often treated with fresh ore or with the products of another operation, the object in all cases being the removal of the base impurities present with the least possible expenditure of fuel and loss of copper. The stability of the copper sulphide and the easy reduction of the copper oxide as compared to the similar compounds of other elements present are the basis of the method pursued. The operations are sometimes more and sometimes less numerous than above indicated depending upon the nature of the ores and the necessity for economy in working.

Bessemerizing Copper "Matte." In this country in the past ten years the practice of Bessemerizing the copper "matte" has become very general. In this operation the principle of the Bessemer steel converter is applied to the purification of the copper "matte" (sulphide of iron and copper). The "matte" in the liquid state is run into the converter and the blast of air turned on. The liquid condition of the contents is kept up by the heat resulting from the combustion of the iron and sulphur by the oxygen of the air.

The iron oxide forms a slag with the siliceous lining of the converter and is thus removed; the sulphur is oxidized and passes off as sulphur dioxide. In this country it is usual to pass from the "matte" to "blister" copper by a single blowing, the blow being stopped once or twice to draw or skim off the slag. In accomplishing this result the "matte" must contain about 50 per cent of copper. The charge for the converter may be obtained either by remelting in a cupola furnace the "matte" obtained in the first operation of smelting or by running the "matte" directly from the reducing furnaces to the converter. In the smelter at Great Falls, Montana, the latter plan is in operation. There the converters are directly in front of the furnaces and the general arrangements are similar to those of a Bessemer steel plant.

Under the conditions of our western copper mines the savings of fuel, labor, &c., by the Bessemer modification has caused a very great application of it.

Pyritic Smelting Without Fuel. An attempt which has met with some success, has been made in this country to extend the principle of the converter to the direct reduction of the native ores in blastfurnaces without the use of any carbonaceous fuel. In this process it is aimed to oxidize the impurities of the ore and to develop the necessary heat by this oxidation to remove the impurities themselves and obtain the metal by a single operation in the blast furnaces. The blast furnace is thus made to play the part of a huge Bessemer converter.

The pyritic smelting by the heat resulting almost entirely from the oxidation of the ores employed has been successfully accomplished but it has not been sufficiently developed to determine its probable importance. The term pyritic smelting has been in use a long time and the process just mentioned under this heading differs from previous ones employed, in that the pyritic ores are required to supply the fuel for their own reduction, to act as a menstrum for collecting the precious metal and as a factor in slag production. In the older pyritic reduction the sulphuretted material was merely used as a collector of the precious metals and not for the second and third purposes.

Copper Reduction by the Wet Method. This method depends upon the conversion of the copper in the ores into a soluble form and the precipitation of the copper from solution. The method is in general applied to the ores that are

very refractory or are poor in copper. The copper salts commonly produced are the chlorides and sulphates. The copper oxides or sulphides may be converted into chlorides by roasting with common salt or treating the ore with a solution of ferric chloride or hydrochloric acid. The sulphide ores may be converted into sulphate by carefully roasting or by exposure to air and moisture; such change often occurs in the natural ore beds. The oxidized ores may be converted into sulphates by the direct action of sulphuric acid or by roasting with iron sulphate.

Metallic iron added to the solution of the sulphate or chloride precipitates the copper in metallic condition. The precipitated copper has to be ^{melted} ~~milled~~ and refined.

Electrolytic Refining of Copper and the Extraction of Silver and Gold. In the smelting of copper by fusion as above described any gold or silver that is present in the ore is retained by the copper. In much of the copper produced it is commercially profitable to extract the precious metals. The native copper from Lake Superior is not generally refined for silver or gold, but a large portion of that from Montana, Arizona, and Colorado contains these metals in paying quantities. The Bessemerized or other metallic copper from these sources is now largely refined by electrolysis.

For this purpose the copper is cast into plates about three inches thick weighing 275 or 300 pounds. These plates are made the anodes in decomposing cells, the kathodes being thin sheets of copper themselves formed especially for this purpose ^{of} electrolysis. The electrolyte employed is the sulphate of copper in solution. Under the influence of a powerful electric current the anode plates are rapidly transferred to the kathodes while the gold and silver fall as "slimes" in the vats. The kathode plate being of electrolytic copper the entire mass of metal at that plate is deposited copper. This process gives copper of a high degree of purity but it is not equal to the native copper.

The deposited copper has to be subjected to fusion to destroy its crystalline texture before it is fit for industrial purposes. The "slimes" are subjected to the action of dilute sulphuric acid by which the copper is dissolved out—the residue is fused and the gold and silver separated either by electrolysis or by dissolving the silver out with sulphuric acid. The silver sulphate is reduced by metallic copper or iron.

Separation of Silver from Copper "Matte"; Ziervogel Method.

This method depends upon the fact that by carefully roasting the argentiferous copper "matte" (sulphides of silver, gold, and iron) the silver may be left as a sulphate while the iron and copper are converted into oxides, their sulphides being first formed and then decomposed. The sulphide of silver can then be dissolved out from the two oxides. The silver is precipitated from the solution by metallic copper.

2. ^{gru}*Lignation Process.* The crude copper before refining is sometimes subjected to the lignation process for the separation of the silver. In this process the argentiferous copper is fused with about three times its weight of lead. The lead alloyed with the silver is much more fusible than the copper and by careful cooling this rich alloy may be nearly entirely separated from the copper. The silver is then separated from the lead by cupellation.

Properties of Copper. Copper is a valuable metal in the arts. Its specific gravity is about 8.9, a little lower than iron. It is very malleable, ductile, and tenacious. Among the common metals it is next to gold and silver in malleability, and next to iron in tenacity. It fuses at a lower temperature than iron. It is one of the best conductors of heat and electricity. Its ductility, malleability, and conductivity are greatly diminished by even minute quantities of impurities. Copper is only slowly affected by exposure to dry air at common temperature. In the presence of the moisture and carbon dioxide of the air, it becomes covered with a green carbonate commonly but improperly called verdigris.

Dilute hydrochloric and sulphuric acids do not act upon copper if air be excluded. Hot sulphuric acid acts readily upon it. Nitric acid in any form acts upon it, though the

presence of nitrous acid is said to be necessary to begin the action.

Uses of Copper. Copper is used very extensively, the most important use being in the construction of electrical machinery and apparatus, for the manufacture of boilers, chemical stills and apparatus, kitchen utensils, cartridge cases and as sheathing for vessels. In sea water the copper is corroded, due to the formation of the oxychloride. This roughens the surface and gives points of attachment for barnacles and other salt water forms, which often greatly impede the sailing power of vessels, many tons of these animals having been removed from a single vessel. Numerous attempts have been made to protect this sheathing from corrosion.

Cooking utensils of copper should always be kept perfectly bright to avoid the formation of poisonous salts by the acids of food. Even then the joint action of the air and the vegetable and other acids often present may contaminate the food. This fact justifies the custom of coating the interior of such vessels with tin. Copper is also used in making electrotypes and as a constituent of many useful alloys. Bronze is composed of copper and tin and brass of copper and zinc.

Compounds of Copper. The Oxides. Among the compounds of copper employed otherwise than as ores may be mentioned the black and red oxides (CuO and Cu_2O). The first is employed as a source of oxygen in organic analysis; the second is used in glass making, to impart a red color.

Copper Sulphate. Copper sulphate may be prepared by dissolving copper in sulphuric acid or by the oxidation of copper pyrites. It is very largely employed in solution in forming electrotypes and in galvanic batteries. It is also largely employed in dyeing, in calico printing, and in the manufacture of pigments.

Carbonates of Copper. The native carbonates of copper when found in massive forms yield the minerals known as azurite and malachite used in ornamental work. They are also used as pigments.

Some of the other compounds of copper find limited application. The hydrated oxide dissolved in ammonia known as "Schweitzer's reagent" yields a solution which dissolves cellulose. The cupric chloride finds some application in calico printing and in the manufacture of colors.

SILVER; Ag; 108.

Occurrence. Silver is a pretty widely diffused metal, though it occurs only in small quantities. It is found in the metallic state; its principal ores are the sulphide, the sulphide in common with the sulphides of arsenic and antimony, the chloride, the iodide, and the bromide. All these are very generally associated with the sulphides of iron, lead, and copper. The sulphide is the ore yielding the most silver.

Reduction of Silver From Its Ores. Silver being one of the precious metals and its ores being very varied and generally associated with a large per cent of other material its metallurgy is very varied. The processes for obtaining the metal may be classed under three heads: 1st, Smelting; 2nd, Amalgamation; 3rd, Leaching.

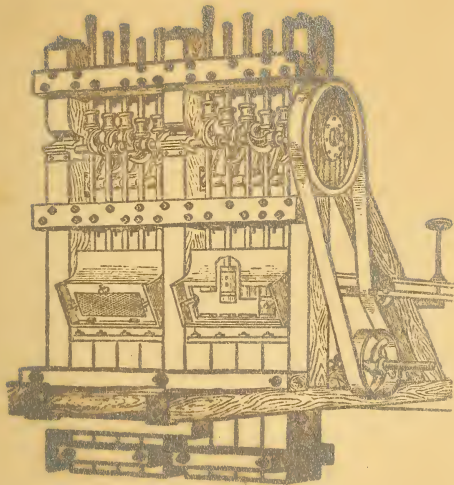
Smelting for Silver. This process is applicable to the ores of silver which accompany the ores of lead and copper, these last named compounds being present in sufficient quantity to render their extraction possible and profitable by smelting. The success of the process depends upon the fact that in the operation of smelting and separating the lead and copper from the baser matter of the ore, the silver remains with the lead or copper. It may be said that when the silver ores are smelted with the ores of lead and copper that the silver ore is reduced with the ores of these metals and the silver dissolved and carried down by the lead or copper. The smelting of silver ores associated with lead and copper

ores is conducted on a large scale in this country. The manner of reducing the lead and copper ores has been described under those metals and the methods of refining these metals for obtaining the silver are also there described. These processes therefore include silver smelting. From the lead and copper ores of Colorado and from the copper ores of Arizona and Montana there is a large yield of silver.

Amalgamation Process. This process depends upon the fact that mercury will reduce certain compounds of silver and that it dissolves or amalgamates metallic silver. The method is applied to a great variety of ores which, from their mineral associates or lack of fuel can not be economically smelted. The process is an old one and many slight variations in the details of the process exist. The method most generally adopted in this country is known as the Washoe or "pan" process; it has been and is still largely employed in the West.

If the silver exists in the ores in such form that they are readily amalgamated the process is largely one of mechanical detail. Such ores are in this country termed "free milling," and the steps in the process are as follows: The ore is first crushed in a mortar by stamps. The stamping involves the principle of the pestle and mortar; there are usually four or more stamps in operation in each mortar.

In California a single mortar with its stamps is called a "battery." In the sides of the mortar are placed screens with the proper number of meshes and when the ore is sufficiently crushed it is carried through these screens by a stream of water flowing through the mortars. The mud from the mortars is charged into iron pans and ground to a fine pulp and amalgamated with mercury. The charges from the amalgamating pans are passed into tanks in which the mercury and amalgam are separated from earthy matters. The free mercury is then separated from the amalgam by straining and the latter subjected to distillation, the



mercury passing off and the silver being left behind. The mercury is of course collected for future use. The direct process is especially applicable to ores rich in native silver, silver chloride, and not an excess of silver sulphide.

Sometimes the ores rich in the sulphide are subjected to preliminary treatment before amalgamation. They are roasted with common salt by which they are converted into the chloride. The amalgamation then takes place directly, the mercury reduces the silver chloride and the reduced silver combines with another portion of the mercury—the amalgamation is frequently accomplished in barrels. $\text{AgCl} + 2\text{Hg} = \text{HgCl} + \text{AgHg}$. This method was employed with certain ores of the Comstock Lode rich in silver sulphide and was formerly employed at other places but it is not now much used in this country.

The ores from the great Comstock Lode of Nevada were mainly reduced by the pan process. The mechanical appliances in such works are generally very extensive and consist of (1) the crusher, (2) the stamps, (3) pans for grinding and amalgamating, (4) settlers for removing the settlings and amalgams from the pulp, (5) the agitators which are supplementary to the latter, (6) appliances for saving "slimes" and "tailings," (7) retorts for sublimation. The crusher breaks the ore when necessary into lumps. The stamps are heavy iron pestles lifted and dropped by machinery in iron mortars where the lump ore is crushed. A stream of water flows through the mortar and carries with it the pulverized ore. This water flows into tanks where it deposits the bulk of the earthy matter. The water flowing from the tanks always carries certain very fine material which is subsequently collected under the name of "slimes." From the tanks the crushed ore is conveyed to pans for grinding and amalgamation. These pans are generally iron tubs about three feet deep and from four to six feet in diameter. They are arranged to grind the sand very fine and to thoroughly mix it with the mercury, the grinding taking place mainly before the addition of the mercury. The settlers are tubs of iron or of wood with iron bottoms. In the settlers the pulp is diluted with water and the whole agitated to separate the mercury and the amalgam. The separation is still further accomplished in the agitators. The amalgam and mercury thus obtained are thoroughly washed, strained through canvas to separate them, and the amalgam distilled. The earthy matter from the settlers and agitators is called "tailings," both the "slimes" and "tailings" contain some silver and are sometimes subjected (the

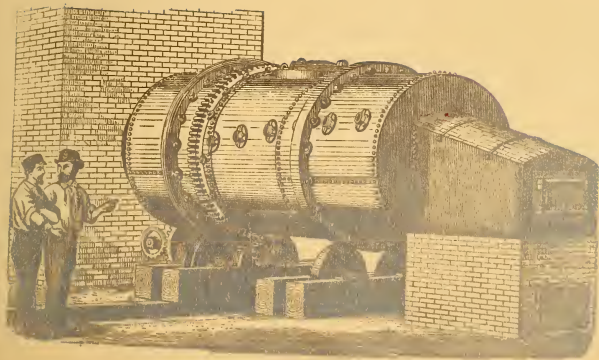
former always) to a second treatment. The above process gives the principal steps in the production of "free-milling" ores; in all such operations in the West there is universal practice of adding certain chemicals to the charge in the pan. The so-called chemicals are sodium chloride and copper sulphate. The action of these chemicals is uncertain and by some good authorities their beneficial effect is doubted. It is thought most likely to be represented by the following reactions. $2\text{NaCl} + \text{CuSO}_4 = \text{Na}_2\text{SO}_4 + \text{CuCl}_2$; $2\text{CuCl}_2 + \text{Ag}_2\text{S} = 2\text{AgCl} + 2\text{CuCl} + \text{S}$; $2\text{CuCl} + \text{Ag}_2\text{S} = 2\text{AgCl} + \text{Cu}_2\text{S}$; $\text{AgCl} + 2\text{Hg} = \text{AgHg} + \text{HgCl}$.

When the ore is stamped without preliminary treatment it is known as wet stamping. In wet stamping the crushed ore is carried from the mortars through the screen by running water. When the ores are subjected to a preliminary drying or roasting with or without salt the process then involves *dry* stamping. In the dry stamping the crushed ore is driven through the screens by the impulse communicated by the stamps. In this case the front of the screen is enclosed by dust-tight boxes and special arrangements are made for removing the crushed ore from the boxes. Dry stamping is now principally used with the leaching process yet to be described. The drying and roasting necessitate of course different additional appliances at works to accomplish these results. The roasting of ores in our western country is almost entirely effected in some form of mechanical furnace.

There are two types of these furnaces, the horizontal rotating and the vertical shaft. The Brückner ~~reducing~~ cylinder may be taken as an illustration of the first. This cylinder is from twelve to sixteen feet long and five to seven feet in diameter, composed of iron shells; the whole is lined with brick. Passing through the cylinder from side to side is a number of pipes which form a sort of diaphragm. One end of the cylinder fits into a fire-box and the other into a chimney. The flame from the fire-box is made to play through the cylinder. The cylinder revolves about its longer axis and the motion, in connection with the diaphragm, keeps the ore properly exposed to the action of the fire.

The vertical furnace is a small shaft furnace surmounted by a charging apparatus which is operated mechanically and which feeds the ore to the furnace with the greatest regularity and exactly as demanded. The Sledefelt is the commonly used furnace of this type.

Leaching Process. This process is applicable to ores of silver which either from their nature or motives of economy



can not be treated by smelting or amalgamation. It is generally practiced upon poor or what are called "rebellious" ores from the difficulty of working them by other methods. It depends upon the fact that certain silver compounds can by difference of solubility, be separated from accompanying minerals and then the silver obtained by simple treatment. The method usually followed in this country (that of Von Patera) is to roast the silver ore, generally silver sulphide, with common salt by which the silver is converted into the chloride. The roasted ore is then leached with water to dissolve out such substances as are soluble in that liquid. It is then leached with some solvent generally sodium or calcium hyposulphite which dissolves the chloride. The silver may then be precipitated as silver sulphide by adding calcium or sodium sulphide. The silver sulphide is then roasted and cupelled.

In this process the ore is first dried, crushed by dry stamping or rollers, and then roasted with sodium chloride.

The roasting is done in the Brückner cylinder already described. Mr. Russell has modified the process by leaching a second time with a mixture of sodium and copper hyposulphite (made by adding copper sulphite to sodium sulphite). The second leaching dissolves out native silver and the sulphide of silver. To this solution he adds a solution of sodium carbonate which precipitates the lead salts as lead carbonate; the lead salts may be thus separated. The subsequent operations are as described in the Von Patera process. The Russell process is applicable to ores and "tailings" containing the native metal, the sulphide, and greater quantities of the baser metals than can be satisfactorily worked by the Von Patera process.

In the old Freiburg method the roasted silver ore is agitated with scrap iron and mercury in barrels. The iron reduces the chloride of silver and the metal then combines with the mercury. The amalgam is heated in a retort to separate the silver. The Ziervogel process of separating silver from copper "matte" (described under copper) involves the leaching of the silver sulphate from a "matte" prepared by fusion. It therefore is not here included under the leaching process, though it is sometimes so classed.

Properties of Silver. Silver has been known from remote antiquity. Its general appearance is familiar to every-

one. It is slightly harder than gold and softer than copper. Its specific gravity varies slightly with mode of preparation but is about 10.5. Next to gold it is the most malleable metal. It is very ductile, one grain may be drawn into a wire 400 feet long. It contracts in solidifying from the molten state. It is the best conductor of heat and electricity. It fuses at about 950°C . and can be distilled without difficulty. Molten silver absorbs over twenty times its volume of oxygen which is given off with the exception of seven-tenths of one volume on cooling.

It is not oxidized in the air, dry or moist, at any temperature, though it is oxidized by ozone. It is tarnished by hydrogen sulphide in the presence of air with the production of silver sulphide. Pure hydrogen sulphide does not attack silver. This tarnish is readily removed by potassium cyanide. It is readily acted upon by nitric acid with the production of silver nitrate. Hot concentrated sulphuric acid acts upon it with the formation of the sulphate. Boiling hydrochloric acid acts upon it. It resists the action of fused alkaline hydroxides better than platinum and is consequently more frequently used in the laboratory for crucibles, &c.

Uses of Silver. The principal uses of silver are for coin, jewelry, photography, and for silvering other metals and alloys. The coin of the United States is composed of nine-tenths silver and one-tenth copper; for all other useful purposes it is similarly hardened. The plating of articles may be accomplished by electrolysis or silver leaf may be charged upon the properly prepared plate by burnishing. Silvering may also be accomplished by treating with an amalgam of silver, then heating to separate the mercury. The chloride of silver with certain reducing salts is likewise used to yield a film of silver.

Frosted silver is prepared from standard silver by heating to oxidize the copper and then dissolving out the oxide

by dilute sulphuric acid, this gives a surface of nearly pure silver and with a blached, frosted appearance.

The so-called oxidized silver is produced by immersing silver in a solution made by boiling sulphur in a solution of caustic potash. It is really the sulphide of silver.

Pure silver may be obtained from the standard silver by dissolving the piece in nitric acid and precipitating the silver from the solution in the form of the chloride by the addition of a soluble chloride. The silver chloride may then be washed until all the copper salt is removed and heated with sodium carbonate, $2\text{AgCl} + \text{Na}_2\text{CO}_3 = \text{Ag}_2 + 2\text{NaCl} + \text{O} + \text{CO}_2$.

Compounds of Silver; AgNO_3 . In addition to the ores of silver already mentioned there is a large number of compounds, the most important of which is the nitrate. The nitrate is prepared by dissolving silver in nitric acid, evaporating to crystallization and then fusing to expel free acid. It is used as a cautery in surgery and for this purpose it is usually cast into small cylindrical sticks. Its caustic properties depend upon the facility with which it gives up its oxygen. It readily yields its oxygen to organic matter with the deposition of black metallic silver. There is nearly always sufficient organic matter in the air to cause the nitrate to blacken after exposure for a short time. This property accounts for the use of the nitrate for marking ink and as a constituent of certain hair dyes. The nitrate is the essential constituent of common indelible ink and the permanent marking is due to the deposit of the finely divided silver in the fibre of the cloth. The nitrate is very largely used in the preparation of photographic plates. Stains upon the skin from the nitrate may be removed by solution of potassium cyanide or tincture of iodine.

Silver Chloride; AgCl . This compound is always produced and precipitated when a soluble salt of silver meets a soluble chloride in solution. The precipitate is at first white,

then violet, and then black. The blackening is hastened by the action of sunlight or the presence of organic matter. The change of color is due to the conversion of the chloride into the sub-chloride. The chloride is readily soluble in ammonia or in potassium cyanide. The chloride is generally the form to which the silver is brought for extraction from the ores by leaching and in some of the amalgamation processes.

Reactions of Silver Salts. A silver salt in solution yields a white curdy precipitate of silver chloride whenever a soluble chloride is added. The precipitate is insoluble in nitric acid, blackens by exposure to light, and is soluble in solution of ammonia. Solutions of silver ^{salt} are reduced to the metallic state by iron, copper, zinc, and other baser metals.

MERCURY.

Occurrence. Mercury occurs in small quantities in the metallic state, but the principal ore and source of mercury is the natural sulphide, cinnabar HgS . Metallic mercury frequently occurs disseminated in minute globules through the cinnabar. The chief mercury mines are those of Idria in Austria, Almaden in Spain, New Almaden in California, and other mines near San Francisco.

METALLURGY OF MERCURY.

The principle of the extraction of the mercury from the sulphide is simple and requires only the removal of the sulphur and volatilization and condensation of the mercury. To accomplish this result most economically on a commercial scale involves an extensive plant.

Only two methods have been employed in the reduction; 1st, The oxidation and removal of the sulphur of the ore by ignition in the air, $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$. 2nd, By heating the ore with some base as lime or iron scales by which the sulphur is removed mainly as the sulphide of lime or iron. The second method is seldom employed and will not be described.

Roasting. The metal is now generally extracted from the sulphide by roasting the ore in shaft furnaces the operation being a continuous one. The spent ore is removed at the bottom and fresh ore fed in at the top of the furnace. The air for the oxidation of the sulphur is frequently heated before admission to the furnace. For this purpose the heat given out in the condensing chambers is most generally employed, the air being lead through these chambers in pipes. During the roasting the sulphur is converted into sulphur dioxide and the mercury volatilized; all the important roasting furnaces in this country are in fact shaft furnaces. Those which depart from the vertical shaft form consist of a series of parallel inclined channels built upon a natural slope. The channels take the place of the shaft. The ore is fed in at the top and the fire-place is at the bottom.

Condensation. With the modern American continuous roasting furnaces the sulphur dioxide, the volatilized mercury, and other products from the furnace are conducted into a series of condensers so extended as to cause the condensation of all the mercury before the products are permitted to escape into the air. These condensers consist of a series of chambers so connected that the vapors from the furnace shall pass through them all, the mercury being condensed and retained in the chambers. The chambers are so constructed that the mercury is gradually brought together by virtue of its fluidity and is removed from the chambers at necessary intervals. These chambers are made of iron, brick, glass, or wood and a plant frequently includes two or more kinds of chambers. Beyond the chambers proper, wooden channels often extend for hundreds of feet and the gases finally make their exit through a long flue.

Purification of Mercury. Mercury may be purified from common metals by distillation. It may also be purified by treating it with dilute nitric acid. From mechanical im-

purities it may be freed by forcing it through chamois leather; this also removes some of the metallic impurities. The same result is effected somewhat less perfectly, by filtering through a cone of paper with pin-hole aperture. Mercury in this country is put up in iron flasks at the mines, the flasks weighing 76.5 pounds when filled.

Properties of Mercury. With the exception of the rare metal gallium, mercury is the only metal liquid at the ordinary temperature. As a liquid it is remarkable in that it neither wets nor adheres to solids, except those metals with which it forms alloys. Its specific gravity at 0°C . is 13.59. It solidifies at -38.8°C . and boils at 357.2°C . It is a good conductor of heat and electricity.

It is unaltered in air or oxygen at ordinary temperature but oxidizes when heated to near its boiling point, the oxide being again reduced when heated higher. In air containing hydrogen sulphide it tarnishes. When agitated with turpentine or triturated with powdered chalk or other inert substances, it is converted into a grey powder which is thought to be a mixture of mercury with some oxide. This powder is used in making ointments and pills. Mercury forms an amalgam with all common metals except iron and lead. It adheres to platinum.

Hydrochloric acid does not act upon mercury. Strong sulphuric acid has no action in the cold, but hot it attacks it forming mercurous and mercuric sulphates. Nitric acid attacks it forming mercurous and mercuric nitrates.

Uses of Mercury. Mercury is used in the construction of thermometers, barometers, and other physical apparatus. It forms an amalgam with gold and silver and is largely used for the extraction of these metals from their ores. Its use for this purpose is improved by adding to it a little sodium or potassium. Many of the amalgams are used in the arts the most important being the amalgam with tin used in the

manufacture of mirror glasses; this amalgam consists of about one-fifth mercury. The mercury is placed on a level surface of tin-foil and the glass carefully slid on to remove the excess of mercury. The plate is then subjected for several days to considerable pressure by which the amalgam is made to adhere to the glass.

The mixed amalgam of cadmium and copper or gold, and of gold, silver, and tin are used in dentistry.

Mercury in the form of vapor, or finely attenuated, will produce mercurial poisoning but when swallowed in sensible masses its injurious effects are believed to be mechanical rather than chemical.

Compounds of Mercury. Mercury forms two classes of compounds, mercurous and mercuric. In the first it acts as a univalent and in the second as a bivalent element toward other elements. Only the most important of these compounds will be mentioned.

Cinnabar; HgS . It has already been stated that the native sulphide is the source of all the mercury; the artificial sulphide is largely prepared and used as a pigment. The native sulphide does not yield the pigment. The artificial sulphide is prepared in two ways, the dry and the wet. By the first the proper proportions of the mercury and sulphur are agitated together and the black sulphide of mercury thus obtained is sublimed. In the wet process the black sulphide of mercury is produced by precipitation and this is converted into the red sulphide by sublimation or by the long continued action of alkaline sulphides upon it. The red and black sulphides have the same composition and the change from one to the other is not chemical.

Mercuric sulphide is not soluble in either of the three great mineral acids at ordinary temperature. It resists the combined action of the air, carbon dioxide, aqueous vapor, and light. These facts explain the permanence of vermilion colors.

Chlorides of Mercury. There are two chlorides of mercury each of which is of considerable importance.

Mercuric Chloride; Corrosive Sublimate; $HgCl_2$. This ~~sulphide~~ ^{chloride} is produced when the vapor of mercury is burned in chlorine gas. On a large scale it is prepared by distilling mercuric sulphate with common salt, the chlorine ^d sublimes, sodium sulphate being left behind, $2NaCl + HgSO_4$ (heated) $= Na_2SO_4 + HgCl_2$. Corrosive sublimate is quite soluble in hot water but much less so in cold. Its solution is extremely poisonous. It coagulates albumen forming with it an insoluble compound which strongly resists putrefaction. For this reason it is largely used by naturalists in the preparation and preservation of specimens. Its action on albumen makes this substance an antidote, if properly administered, in case of accidental poisoning. Wood impregnated with a solution of corrosive sublimate is protected from decay and the attack of parasites. Its use in the preservation of wood is now largely superseded by creasote.

Mercurous Chloride; Calomel; $HgCl$. This substance is insoluble and is therefore produced whenever a soluble mercury salt meets a soluble chloride in solution. This salt can be manufactured by adding mercury in the proper proportion to the reagents used in the manufacture of corrosive sublimate when the calomel is produced instead of the sublimate. This is the principal salt of mercury used in medicine.

Mercury Oxides. Mercury forms two oxides, Hg_2O and HgO , the latter commonly known as the red oxide is the more important. This oxide is formed when the mercury is highly heated in air. It is used under the name of red ointment and when thoroughly incorporated with certain ingredients constitutes a poisonous ointment sometimes used to destroy the parasites which affect animals. It is prepared for this purpose by decomposing the nitrate of mercury by a

gentle heat or better by adding a little mercury and de-oxidizing the nitrate, $\text{Hg}(\text{NO}_3)_2 + \text{Hg}_2 = 3\text{HgO} + \text{N}_2\text{O}_3$. The oxide parts readily with its oxygen and is therefore sometimes used as an oxidizing agent in the laboratory.

PLATINUM.

Occurrence. No compound of platinum with a non-metallic element has been found in nature. It is always found in the metallic state but always alloyed with the other metals. The metals usually present belong to the platinum group and are rhodium, iridium, osmium, ruthenium, and palladium; these metals usually occur alloyed with each other and with the platinum. The platinum metals are found in alluvial deposits similar to the deposits containing gold, indeed gold is frequently present.

Most of the platinum is obtained from the Russian deposits in the Ural Mountains, near Goroblagodat; some comes from Brazil, Peru, Colombia, Borneo, and it has been found in the United States, Canada, and Australia. The platinum alloys generally occur in small grains distributed through the sands from which it is separated by washing. The process of separating the platinum from the associated metals is largely a chemical one, it was formerly entirely so. The separation in this process was brought about by the action of aqua regia upon the native alloy and depends partly upon the relative action of the strong and weak acids upon the different metals and partly upon the different properties of the chlorides produced. The platinum has also been separated by smelting the ore with galena. The lead forms an alloy containing nearly all the platinum from which it is separated by cupellation.

Properties of Platinum. With the exception of osmium and indium platinum is the heaviest of the elements, its specific gravity referred to water being 21.5. It is 23400 times as heavy as hydrogen. It is the most infusible of the

metals. It can be readily melted by the oxy-hydrogen flame and by this means it can be made into vessels. It is not affected by the air at any temperature, nor do any of the acids singly attack it at common temperature. Concentrated sulphuric acid at high temperature acts slightly upon it. It is very malleable and ductile and at high temperature (white heat) is weldable. It possesses the power of causing the combination of oxygen with other gases or vapors.

It is dissolved by aqua regia, the fused caustic alkalies attack it, as do phosphorus, sulphur, arsenic, and carbon at high temperature. It readily alloys with lead and other easily fusible metals. Care should be taken that these substances be not heated highly in platinum vessels.

The action of platinum upon gases may be shown by holding a piece of thin platinum foil in the flame of a Bunsen burner until it is red hot, then if the gas be turned off and then be turned on quickly again the escaping gas will keep the metal at a red heat and may even relight it. This result is brought about by the influence of the metal in causing combination between the gas and the oxygen of the air. The temperature of the foil may be too low to emit any light when the gas is turned on, but the oxidation occurring at its surface soon brings it to redness. Spongy platinum (obtained by decomposing the ammonia-chloride of platinum) possesses this actuating power to a higher degree than does the foil.

Dobreiner's automatic lamp is lighted by means of spongy platinum. This apparatus consists of an alcohol lamp in connection with a little automatic hydrogen generator. By pressing a lever a jet of hydrogen flows out and falls upon some spongy platinum. The oxidation that ensues rapidly raises the temperature until the vapor of alcohol from the lamp-wick near the metal inflames. This action of the metal was for a time made use of in the manufacture of acetic acid. The spongy metal caused the rapid transformation of the

alcohol into acetic acid by inducing the oxidation of the alcohol.

The precipitated form of platinum commonly called platinum black possesses this power to a still higher degree; hydrogen is instantly ignited by falling upon it. This form of platinum is capable of absorbing 800 times its volume of oxygen and it absorbs and condenses considerable quantities of other gases. The oxidation caused by it is probably in some cases due to the greater physical contiguity of the gases produced by the condensation.

Platinum is employed in the form of wire, foil, dishes, crucibles, forceps, tongs, retorts, and other laboratory apparatus. Its small coefficient of expansion permits it to be fused into glass without subsequent cracking. Platinum is used in large vessels for retorts and coolers in the purification of sulphuric acid.

Compounds of Platinum. Platinum forms two classes of compounds the platinous and the platonic—in the first it plays the part of a dyad and in the second of a tetrad. The most important of the platonic compounds is the platonic chloride, perchloride, PtCl_4 . It may be prepared by dissolving platinum in aqua regia. This salt is of value in the laboratory because it forms slightly soluble double chlorides with the chlorides of the alkali metals and with certain organic hydrochlorides and thus aids in detecting and separating these bodies.

Other Metals of the Platinum Group. As already stated, the other metals included under this head are palladium, iridium, osmium, rhodium, and ruthenium and they are generally found in association with platinum, alloyed with each other and with it. These metals resemble platinum in their unchangeable nature in air. Iridium is the most useful of this group. It is a hard steel like metal and is used for knife edges in delicate balances and for similar resisting surfaces. It generally increases the hardness of its alloys. Its alloys with platinum are important. The most refractory platinum vessels contain some iridium. These alloys were adopted by the Committee on International Standards for making standard weights and rules.

Palladium is the most fusible of the group, its fusing point being between 1500° and 1700° C. Osmium is the heaviest of the elements yet discovered, its specific gravity being 22.39 to 22.42.

Osmium forms a volatile tetroxide which is very poisonous. The native alloy of osmium and iridium is used to a limited extent for hard

wearing surfaces; this alloy is found most abundantly in Russia, California coming next in order of production.

Palladium possesses the power of absorbing and condensing gases to a remarkable degree and the metal has been used to a limited extent for wearing surfaces in philosophical apparatus.

The salts of this group have found no useful application.

GOLD; Au.

Occurrence. Gold occurs widely distributed in nature though in small quantities. It is nearly always found pure or alloyed with other metals but occasionally combined with tellurium. The natural gold is most usually alloyed with silver but sometimes with copper and other metals. Gold principally occurs in four ways; 1st, Disseminated through the gangue of quartz veins; 2nd, In *alluvial* deposits ancient or modern; 3rd, To these modes of occurrence of gold must now be added that of the South Africa gold fields where the metal is disseminated through "reefs" which were originally *shallow marine* deposits, but now form part of the mainland far from the shore;* 4th, Gold also occurs in small quantities in ore deposits of other metals.

METALLURGY OF GOLD.

The sources from which gold is obtained in commercial condition come under three heads, 1st, From the auriferous ores of the metals; 2nd, From auriferous quartz veins; 3rd, From sedimentary deposits, alluvial or marine.* The processes by which the gold is obtained from these sources may be limited to four as follows: 1st, Smelting; 2nd, Amalgamation; 3rd, Leaching; 4th, Simple washing by water. It is thus seen that the processes employed except the last bear the same names as those employed in the metallurgy of silver and the general method of treatment and the principles involved are very similar.

*Gold has also been found in the sands of certain sea beaches of the present day, notably in California, Oregon, and Australia, and it is known to be present in minute quantity in sea water. At one time attempts which were partially successful were made to obtain gold from the beach sands of our western coast.

Smelting. This process is applied only to the gold from the first source and includes all that gold obtained in the smelting of argentiferous copper and lead containing gold. These processes have been described and it is only necessary to state here that the gold after the smelting, remains with the silver and is separated therefrom by acids or by electrolysis. Gold is thus obtained in considerable quantity at many smelters in this country—notably those in Montana, Arizona, and Colorado. The gold is, however, not the principal product of these smelters.

Gold ore from quartz veins is sometimes crushed and smelted with lead or copper ores, for the purpose of removing the gold, but no additional principle is involved to those already described under the smelting for these metals; but the gold from the quartz veins is almost always separated in the manner now to be described.

Gold from Quartz Veins. In obtaining the gold from quartz veins there are usually involved two distinct processes: 1st, Amalgamation; 2nd, Leaching or lixiviation. To secure as much gold as possible from the ore it is generally subjected in succession to treatment by both processes. Occasionally only the first is employed, but the leaching process is often employed alone. These processes are very similar to the corresponding processes for obtaining silver—they will be briefly outlined. There are several distinct steps in each of the above processes, but the chemical principles involved are simple. The gold bearing rock is first broken and then stamped to a fine state of division in "stamp batteries." These "batteries" are essentially similar to those described for the stamping of silver ores and they consist of an iron mortar and a stamp; the latter are iron rods shod with steel and are lifted and dropped by machinery. They weigh from 700 to 1000 pounds. By these stamps the ore is crushed until it is fine enough to pass through the perforated screens in the side of the mortar.

The proper quantity of water is admitted to the mortar and carries the crushed ore through the screens. Gold mills are always wet stamping.

Amalgamation. The amalgamation may begin in the "batteries" or not until the pulp has passed through the screens. When amalgamation begins in the "batteries" the mortars are usually lined at the ends and on one or both sides with amalgamated copper plates and mercury is charged into the "battery." The mercury amalgamates the gold and a large part of it is caught in the copper plates and inside the "battery." Another portion of the gold is caught by appliances outside the "battery." These contrivances consist of inclined aprons or tables covered with amalgamated copper plates, frequently arranged in descending steps—these plates begin just in front of the screens. The pulp after passing through the screens is carried by the water over the outside copper plates, which catch more of the free gold. The amalgamated copper plates are cleared off at intervals and the amalgam "retorted" to separate the gold; sometimes the amalgam is washed by grinding in a pan before "retorting."

The pulp after leaving the copper aprons is made to flow over blanket-sluices. These sluices are covered with specially prepared mill blankets. The nap of these blankets arrests still another portion of the gold, while most of the sand and lighter minerals are carried over them. These blankets are removed at intervals and washed and the washings are amalgamated in a special apparatus. This amalgam is "retorted" to separate the gold. When amalgamation begins in the "battery" the blanket sluices are less generally used. Whether the blanket sluices are used or not the sands or "tailings" carried away by the water are often subjected to further treatment. These "tailings" may be treated by amalgamation in grinding pans, but they are generally too

impure to be treated in this manner and are subjected to the next process to be described.

Chlorine Leaching. Preliminaries. This process is seldom in this country applied directly to the ores from the mine but is used to obtain the gold which is not caught in the amalgamation operations and which remains with the sands or "tailings." As these sands contain only a small per cent of gold, the first step usually taken is to separate mechanically as far as practicable the gold bearing material from that which carries no gold. This operation is termed "concentration" and is accomplished by the mechanical action of water upon the gold bearing material. The object of "concentration" may be stated to be, to get out of comparatively poor material a comparatively rich one. The process of "concentration" is generally applied to the "tailings" though it is sometimes used to convert a poor ore into a richer one before it is subjected to other treatment.

The gold to which the leaching process is applied is in the metallic state but so intimately associated with other minerals that the mercury has failed to reach it in the amalgamation. The minerals most commonly thus associated with gold in the "concentrated tailings" are sulphides of iron and other metals, the former usually constituting the larger portion. The next step is to roast the "tailings" to convert all the baser metals present into oxides.

Chlorination. The roasted ore is next subjected to the action of chlorine by which gold chloride is formed. The chloride of gold is dissolved out of the chlorination vat by lixiviation with water and the solution received in a precipitating tank. The gold is precipitated from the solution in the metallic form by the addition of ferrous sulphate; the precipitated gold needs only to be fused. The above method of chlorination is known as Platner's process.

Cyanide Leaching. The leaching of "concentrated" ores as well as "tailings" which are comparatively free from

sulphides, is now largely accomplished by treating with a weak solution of potassium cyanide. This in the presence of oxygen forms a soluble compound with the gold from which the metal may be recovered by precipitation by metallic zinc or by electro-deposition.

The principles employed and the general methods pursued in the amalgamation and leaching processes are outlined above, but the number of operations and the details of each vary with the kind and nature of ore. With some varieties of gold quartz so nearly all the gold is obtained by amalgamation that the "tailings" are not worth working. With some ores "concentration" may precede amalgamation instead of the reverse as described above. Sometimes the amalgamation process is preceded by the roasting of the ores and occasionally the ore is such that the leaching process is not preceded by amalgamation. When the ores to be leached by chlorine are rich in silver there is usually added a little salt to the roasting charge and the silver is converted into the chloride. The silver chloride can be dissolved out before the ore is subjected to chlorination. Platner's chlorination process has been modified in this country by Mears so that the chlorine is delivered under pressure into revolving amalgamating barrels. The gas acting under pressure and the agitation and friction of the ore give some marked advantages to this modification but there were at the same time some disadvantages, one of the most marked being the escape of some of the compressed chlorine. Theiss improved on the Mears' method by generating the chlorine in the amalgamating barrel itself, though under less pressure the nascent chlorine was found to be very active and the Theiss barrel method has found extensive application in our western country.

Gold from Sedimentary Deposits. A large proportion of the world's supply of gold has been obtained from sedimentary deposits. In this country the gold from this source is limited to alluvial deposits but in the rich mines of South Africa which have recently come into such prominence, the gold is found in the marginal sea deposits of previous ages which are now tilted and displaced and lie far inland. We shall first speak of the gold from the alluvial deposits of this country.

Placer Mining. The gold from this source in this country is obtained by what is called *placer mining*. The placer deposits exist in the sands along the beds of the present

streams or in the sands and gravels which now occupy the beds of channels and banks of extinct streams. The gold is separated from the sands mainly by the action of water.

When gold was first discovered in California in 1848 a large amount of it was obtained by simple pan-washing. This process was followed by cradle washing and then by sluice working. As the shallow placers were exhausted and the working was extended to the deep placers of former river channels, hydraulic mining was developed. By this means it became possible to economically wash very large masses of earth, in several places several million parts of earth were worked to obtain one of gold. The large amounts of water and earth thus handled required very extensive appliances. The sluices were made from a few hundred feet to several thousand feet long. The great difference between the specific gravity of the gold and the sands (19.3 and 2.6) rendered separation by washing possible, but amalgamated copper plates, riffles and mercury were used in the sluices to more perfectly catch the gold as the operations were extended. In these deep placers the richest sands were generally near the bed rock of the stream and sometimes were so consolidated that they had to be "weathered" or crushed before washing.

In some places the deep placer deposits extended under rock formations that could not be removed. This led to drift mining. The auriferous sands from these mines were often found so consolidated that they had to be subjected to the milling and amalgamation process already described.

Africa Gold Mines. The great mines of the Rand in South Africa deal with gold occurring in a hard conglomerate which was originally a marginal sea-deposit. These deposits were tilted and displaced and now form part of the interior highlands of the country. The sheets in which the gold occurs are called "banket reef." These reefs are mined exactly as are quartz veins. The ore is crushed in stamps and treated by the amalgamation process above described. The amalgamation is begun in the mortars. The "tailings" are "concentrated" and subjected to the chlorination or cyanide process of leaching as already described, the cyanide process being the more common.

Properties of Gold. Gold is a metal of great antiquity and has from the earliest times been esteemed a precious metal. In a pure state it is only about as hard as lead. It is the most malleable and ductile of metals. Its specific gravity is 19.3. For commercial purposes gold is always alloyed with some other metal to increase its hardness and durability, silver and copper being the metals most generally employed for this purpose. The gold coin of the United States is nine-tenths gold, and one-tenth copper alone or an alloy of copper and silver. The purity of gold is generally indicated by carats; pure gold is 24 carats fine. Gold of 18 carats is only three-fourths fine. On account of its great malleability gold leaf can be made exceedingly thin.

Gold is not affected by the atmosphere or moisture and does not tarnish. It is not acted upon by any of the ordinary acids but it is attacked by aqua regia or free chlorine. Common gold alloyed with copper may be made to present a pure gold surface by heating and oxidizing the copper and dissolving it out with sulphuric or nitric acid. The uses of gold are too well known to require mention.

COMPOUNDS OF GOLD.

Gold Chloride; AuCl_3 . The most important of the inorganic salts of gold is the gold chloride, AuCl_3 . It can be prepared by acting upon gold with aqua regia. The chloride is very easily reduced to the metallic state. Organic matter generally, and nearly every substance capable of combining with oxygen will reduce it. The property of the salt together with the permanency of the deposited metal renders the chloride useful in photography.

Oxides and Sulphides. Three oxides of gold have been obtained but they are of no practical importance. Several combinations of gold with sulphur have been obtained but their compositions are not well determined and they are not of practical importance. The *Purple of Cassius* produced when stannous and stannic chlorides are added to dilute solutions of gold is used in enamel painting and in coloring glass. It gets its name from the discoverer, Andreas Cassius of Leyden. The exact composition of this substance is not known but it contains gold, tin, and oxygen.

ORGANIC CHEMISTRY OR CHEMISTRY OF THE CARBON COMPOUNDS.

CHEMISTRY OF THE CARBON COMPOUNDS.

The term "organic chemistry" was formerly used to denote the chemistry of compounds found in the bodies of plants and animals. It was originally thought that these compounds could only be produced in living organisms, animal or vegetable, and that their production was due to the vital forces which were different from the chemical forces artificially brought into play in the laboratory. This view led to the separation of chemistry into two branches of organic and inorganic—the latter including the chemistry of those compounds whose existence in no way depended upon the "vital forces."

The assumption as to the action of the different forces in the organic and inorganic worlds was rendered untenable when it was shown that many organic compounds could be formed by the direct combination of elements or the transformation of inorganic compounds. The preparation of urea accomplished in 1828 by Wöhler, was the first step in the artificial formation of organic compounds from their inorganic constituents. Many organic compounds of great complexity have since that date been built up from the elements themselves and it is now universally recognized that the chemistry of the organic compounds is but a part of the general science of chemistry.

Organic compounds all contain carbon, and organic chemistry is really the chemistry of the carbon compounds but on

account of the large number of such compounds it is convenient to study them separately rather than in connection with the element carbon. For the sake of convenience the division of chemistry into two branches is still generally retained, though the original reasons for the separation have been shown to be erroneous.

There is however a distinction between organic compounds and organized bodies. The former have a definite chemical composition, many of them can be produced artificially and possess definite chemical and physical properties; organized bodies consist of mixtures of definite compounds and have only been produced under the influence of vitality. The chemical relations of the organized bodies and the life processes which go on in them, are treated under physiological chemistry.

CLASSIFICATION OF CARBON COMPOUNDS.

The compounds of carbon outnumber the compounds of all the other elements taken together. The elements most usually combined with the carbon in these compounds are hydrogen, oxygen, and nitrogen. A large number contain only carbon and hydrogen; a still larger number consist of carbon, hydrogen, and oxygen; many consist of carbon, hydrogen, and nitrogen; and still others of carbon, hydrogen, oxygen, and nitrogen. In addition to the four elements named, sulphur and phosphorus frequently occur. In the carbon compounds from organic sources the above named are the elements generally found, but almost all the elements, metals and metalloids have been artificially introduced as constituents of these compounds and some of the metals are found in the natural compounds. The classification of carbon compounds like all other classifications, is based upon similarity of properties and characteristics of the bodies grouped together.

The nature of the carbon compounds permits a much

more perfect classification than is possible in the inorganic chemistry. The members of the same class and the different classes are derivable from each other by comparatively simple reactions.

The system of classification includes nearly all artificially prepared carbon compounds and the greater proportion of those produced in living bodies, but there are many compounds formed in the vital processes of plants and animals whose chemical relations are not sufficiently known to permit their classification, such are the alkaloids and the albuminoids yet to be mentioned.

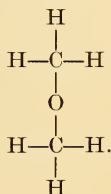
The compounds of carbon are usually grouped into thirteen classes based upon their rational or constitutional formulæ, that is the formulæ which indicate the radicals that compose the compound. There are other classes whose rational formulæ are not made out, based upon certain similar characteristics.

There are a great many carbon compounds which contain only carbon and hydrogen and most of the other well defined carbon compounds can with reason be considered as derived from these, so that the compounds of carbon included under the term "organic" are generally derivatives of those containing only carbon and hydrogen known as hydrocarbons. It is not the purpose of this text to consider the varied relations between the different classes nor between the members of the same class of the carbon compounds, and the classification of the compounds described will only be referred to when such reference helps to define and elucidate the characters which it is sought to set forth.

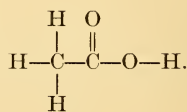
The most general divisions of the carbon compounds which include all those just referred to, are the fatty and aromatic groups. The bodies which make up the first group are derivatives of the hydrocarbons whose general formula is C_nH_{2n+2} (paraffin series); the second group is derived from the benzene series whose general formula is C_nH_{2n-6} . These two groups, fatty and aromatic, are very convenient for general reference.

STRUCTURAL OR CONSTITUTIONAL, AND RATIONAL FORMULÆ.

The basis for the classification of organic compounds is usually partially represented in their chemical formulæ. Such formulæ have already been referred to as structural formulæ but it will be of convenience hereafter to state somewhat more fully the significance of these formulæ. By the careful consideration of the changes and the behavior of any chemical compound under a large variety of dissimilar circumstances it is believed that the order of combination of the atoms in the molecule in many such compounds has been determined. A formula which gives the fullest knowledge as to the constitution of a compound is called its structural or constitutional formula. By such formula it is intended to indicate the connection between the atoms in a molecule. It should be kept in mind that the representation of the formula on paper is of no importance as the formulæ are intended to express the manner of combination and not the actual positions of the atoms themselves. Thus the constitutional formula of methyl-alcohol is determined to be



and of acetic acid is



A rational formula is one that from the way in which it is written, indicates the manner in which a compound breaks up or is formed under certain conditions, or shows the relations of allied compounds to each other. It is an abridged constitutional formula which indicates certain relations not shown in an empirical or molecular formula; or it is a molecular formula so written as to indicate certain chemical relations of the compound. Thus the formula for acetic acid may be written $\text{C}_2\text{H}_3\text{O}_2\text{H}$ to show that the acid is monobasic

or it may be written C_2H_3O,HO which indicates the origin of the acid from certain salts. Since a compound may split up into different groups or radicals or may be formed in different ways the same body may often have a number of rational formulæ each of which indicates certain characters under certain conditions. This fact has already been illustrated in the supposed constitution of certain inorganic salts, but owing to the larger number of atoms in many organic compounds the principle of resolution into rational formulæ is much more frequently possible.

Isomerism and Polymerism. Isomerides or isomeric bodies are those bodies which have the same percentage composition and molecular weight but show different properties. Those isomerides which differ in physical properties but whose transformation under the action of the same agents closely resemble each other are called "isomers." Those isomerides which exhibit dissimilar transformation under similar circumstances are called "metamers." The phenomenon of isomerism is only explicable upon the supposition that the arrangements of the atoms in the molecules are different.

Polymeric bodies or "polymers" are those which have the same percentage composition but different molecular weights and consequently different molecular formulæ. The carbon compounds furnish many examples of isomers, metamers, and polymers.

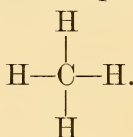
HYDROCARBONS.

Of the carbon compounds the simplest are those containing only hydrogen and carbon and from these, as already stated, most of the others can be derived. The hydrocarbons furnish several series of compounds and each series under the action of reagents yields derivatives so that the possible number of carbon compounds is very great. These compounds frequently exhibit a characteristic not common among inorganic bodies—their molecules contain a large number of

the atoms of the elements which enter them, thus rendering possible a great number of isomers.

SATURATED HYDROCARBONS.

Paraffin Series; Formula C_nH_{2n+2} . The only hydrocarbon containing but a single atom of carbon is methane or marsh gas. Carbon being a tetrad and hydrogen a monad it is evident that on the theory of valency the constitutional formula of marsh gas must be represented thus



indicating a saturated compound or one in which there are no free units of valency. A consideration of the formula above given will show that the relation between the number of atoms of the two elements is such that there are no free affinities. The hydrocarbons of this series can not form compounds with other bodies except by substitution, one or more of the atoms of the molecule must be removed to effect the introduction of others. Since hydrogen is a monad and can not act as a connecting atom, it is evident that on the theory of valency the carbon atoms in hydrocarbons must be connected directly to each other. The different ways in which the connection may be made and yet satisfy all the affinities of each element is thought to explain the frequent occurrence of "isomers." In the saturated hydrocarbons it is thought that no two carbon atoms are held together by more than one combining unit of each atom.

Methane or marsh gas is the lowest member of this series, the others containing more than one atom of carbon. The formulæ of the consecutive members of the paraffin series differ from each other by CH_2 , the first four are, methane CH_4 , ethane C_2H_6 , propane C_3H_8 , and butane C_4H_{10} . Such a series is termed an homologous series. The highest known member of this series contains 35 atoms of carbon. The

members of the series up to those containing four atoms of carbon are gases; from four to sixteen they are liquid at ordinary temperatures; those containing a greater number than sixteen atoms of carbon are solid.

Many of the hydrocarbons of the paraffin series occur abundantly in nature. The occurrence of methane as marsh gas and fire-damp has already been referred to.

Petroleum. The great natural source of this group is the petroleum oil which is found most abundantly in this country and in Russia—it is also found in several other countries.

American petroleum consists almost entirely of the paraffin hydrocarbons, some of the benzene group are present in small quantities. The Russian petroleum contains a considerable per cent of the benzene hydrocarbons and their derivatives. The petroleum is mixtures of the various members of these hydrocarbon series which are separated from each other by fractional distillation—a large number of valuable products is derived from them.

In this country the oil wells are connected by pipe lines with the refineries at New York, Baltimore, Pittsburgh, Cleveland, and Buffalo. The lines in some cases are over three hundred miles long and the oil is forced by pumps through the pipes from the wells to the refineries.

At the refineries the oil is subjected to fractional distillation. The products which first come off as the temperature rises, are of course the gaseous products. The more easily condensable of these are collected, liquefied by pressure, and used to produce cold by evaporation—in the manufacture of ice, etc. This product is mainly composed of C_4H_{10} butane and is called cymogene. The names of the commercial products vary at different places—some of the more important in the order of the boiling points are Rhigolene used as an anæsthetic, Petroleum ether used as a solvent for rubber, Gasolene used for enriching coal gas, Naphtha used as the working substance in naphtha engines. Benzine used as a solvent is

largely substituted for turpentine and comes off between 120° and 150° F.; it is entirely different from benzene, the latter not belonging to the paraffin series. Kerosene is the product which distills over between 150° and 300° F. and is the liquid so largely used as a burning oil. It is purified by agitating with acid and in alkaline solution before it is put upon the market. There are many grades of this oil depending upon the color and fire test to which the oil is subjected. The fire tests are in some cases fixed by law and differ in different places. An oil which when heated in an open vessel to 100° F. does not give off vapor enough to ignite when a flame is brought near its surface, is safe under ordinary conditions of use.

The residue of the crude oils after distilling off the kerosene, is subjected to still higher temperature and from it are obtained the lubricating oils and the solid paraffins. The lubricating oils are daily increasing in importance and are now used in immense quantities. The softer of the solid paraffins are called vaselines, of which there is a number of varieties. The more solid wax-like paraffins are present only in small quantities in the American petroleum, less than three per cent; they reach ten per cent in the Burmah petroleum and are very much more in the petroleum from the shores of the Caspian.

The greater proportion of the solid paraffin is prepared from the products obtained from the distillation of carbonaceous shales. Scotland is the centre of the industry. In Germany and Austria large quantities of paraffin are obtained by the distillation of brown coal or lignite. These coals and shales yield also burning and lubricating oils similar to those from petroleum.

Paraffin is tasteless and without odor, insoluble in water but freely soluble in ether. It is largely used as a substitute for sulphur in dipping matches; it is used in the manufacture of candles, in water-proofing and finishing cloths, and

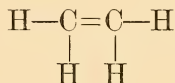
as an insulator in electrical apparatus. It has also been applied to preserve food from deterioration.

Native solid hydrocarbons are found and known under the name of ozokerite. It is used in Europe in the manufacture of candles. It closely resembles paraffin but is thought to contain a smaller per cent of hydrogen.

The petroleum industries of the United States are of immense extent and of vast importance. The burning and lubricating oils furnish one of the largest items of export. The refined oils are exported in tank steamers and a number of these steamers is engaged in such service running between American and European ports.

UNSATURATED HYDROCARBONS.

All hydrocarbons which do not have the formula C_nH_{2n+2} are found to be capable of uniting directly with certain other bodies without the removal of any of the constituent elements, it is therefore assumed that in these hydrocarbons some of the carbon atoms are linked together by more than one unit of valency of each, hence ethene may be indicated thus



and acetylene thus $\text{H}-\text{C}\equiv\text{C}-\text{H}$. In the saturated compounds no atom is connected to any other by more than one unit of valency of each; in the unsaturated two atoms may be connected by more than one unit of each. It is readily conceivable that in these compounds the atoms which are connected by more than one combining unit of each may extend this excess of affinity to other bodies, thus forming new compounds without any change of elements.

Olefine Series. These are unsaturated hydrocarbons whose general formula is C_nH_{2n} . The lowest member of the series is olefiant gas, ethene, or ethylene C_2H_4 . The series

is an homologous one and results by the successive addition of CH_2 .

The first three members of the series are gaseous—most of the remainder are liquid, but the four highest members are solid. The members of this series resemble in properties the corresponding members of the paraffin series—the boiling points of the liquid members which have the same number of carbon atoms lie very close together. This series is obtained from petroleum oil and by the destructive distillation of carbonaceous matter. Ethylene the lowest term of the series, has already been mentioned in connection with carbon—the highest member contains thirty atoms of carbon.

Acetylene Series. The general formula for the series is $\text{C}_n\text{H}_{2n-2}$. Acetylene is the lowest member of the series and the homologues differ consecutively by CH_2 . This series, as the two preceding, consists of gases, liquids, and solids. Acetylene is the only hydrocarbon that can be produced artificially—its production and uses were described under the element carbon.

The terms of the olefine series differ from the corresponding terms of the paraffin series by two hydrogen atoms and the acetylene series from the olefine series in the same manner; the hydrogen in proportion to the carbon growing less in the series in the order named. The latter two series may therefore be considered as derivatives of the paraffin or methane series.

Benzene Series; Aromatic Hydrocarbons. The general formula for the series is $\text{C}_n\text{H}_{2n-6}$ where "n" is a whole number not less than six. The homologues differ successively by CH_2 . On account of the fragrant odor of some of the benzene derivatives they were formerly termed aromatic hydrocarbons, but equally fragrant odors are found among the methane derivatives, hence the term is no longer strictly applicable.

Benzene. The lowest member of the series is benzene C_6H_6 . This body is the basis from which a large number of organic compounds may be derived. Benzene is produced

in the destructive distillation of many organic substances, it is also found in petroleum. It is present in considerable quantity in the more volatile portion of coal-tar oil and this is the source from which it is principally obtained. The light oil from coal tar is subjected to fractional distillation by which the benzene is separated and purified.

It is when pure a thin limpid liquid with an odor suggestive of coal gas. It solidifies at 0°C . It is insoluble in water but mixes with alcohol and ether. It dissolves sulphur, phosphorus, iodine, and many fats and resins which are insoluble in water. It is manufactured in large quantity for conversion into aniline from which are obtained many beautiful and useful dyes. Its vapor constitutes one of the illuminating constituents of coal gas.

Terpene Hydrocarbons. The empirical formula of this group is C_5H_8 . They are volatile oils existing in certain plants; they have not been formed by artificial processes.

Turpentine oil is the most important member of the terpenes, its formula is $\text{C}_{10}\text{H}_{16}$. It exists in the wood, bark, and leaves of many coniferous trees and is generally prepared by distilling the thick juice which is obtained by tapping (making incisions into the bark) the trees. This juice is a mixture of turpentine oil and resin. In this country turpentine is principally obtained from two varieties of the pine the industry being most largely developed in North Carolina.

Turpentine oil when pure is colorless and mobile—it has a penetrating and disagreeable odor. Its boiling point is $158\text{--}160^{\circ}\text{C}$. Its specific gravity is .86. It is but slightly soluble in water but dissolves in strong alcohol, ether, and carbon disulphide. It burns with a smoky flame. It dissolves ^oid^one, sulphur, phosphorus, caoutchouc, resins, and many fixed oils. The consumption of turpentine oil or spirits in the preparation of paints and varnishes is very extensive.

There is a large number of other essential oils belonging to this group which have the same empirical formula and

many of them the same molecular formula as turpentine oil. Such bodies are the oils of lemon, juniper, orange, birch, etc. These oils are generally obtained by distilling the leaves, flowers, seeds, or other vegetable products with water, or by passing a current of steam through these products. The boiling points of the oils are much higher than that of water but they readily distil with aqueous vapor. When the vapors condense the greater portion of the oil forms a layer on the surface of the water and may be entirely separated by shaking the water with ether or saturating it with salt. The ether dissolves the oil and can be separated by distillation. The salt causes the oil to separate. In some of the more delicate perfumes the distillation is accomplished in a vacuum or the oil extracted by pressure or dissolved out by carbon disulphide. These oils when not isomeric with turpentine oil are mixtures of hydrocarbons, having the same percentage composition, with compounds of carbon, hydrogen, and oxygen. By exposure to the air they slowly absorb oxygen and lose their liquid state. They mix in all proportions with linseed, whale, and other fixed oils. The greasy stain communicated to paper by a volatile oil can be entirely removed by heating, which is not the case if it contains a fixed oil.

Camphors. The camphors are crystalline bodies closely related to the terpenes, from which they appear to be formed by oxidation. Common camphor is obtained by distilling the chopped wood of the camphor laurel of China and Japan. It has been produced by the artificial oxidation of several terpenes. Camphor is very slightly soluble in water but readily so in alcohol and ether. It burns with a smoky flame. Its formula is $C_{10}H_{16}O$.

Resins and Balsams. The resins are closely related to the terpenes and appear to result from their oxidation. They are not definite compounds but mixtures, the essential ingredients being certain resin acids, which are rich in carbon and hydrogen and contain some oxygen. The resins are all, with unimportant exceptions, of vegetable origin.

Common resin or colophony is the best example of the class. It is the substance remaining when crude turpentine is distilled and the oil of turpentine expelled. The resins are very widely distributed in the

vegetable kingdom. They are insoluble in water but dissolve in alcohol.

There is a large number of resins used for industrial purposes. Shellac is employed in the manufacture of hats and is the chief constituent of sealing-wax. The many varieties of varnish are prepared by dissolving resins in alcohol. Mastic, dammar-resin and sandarac are some of the common varnish resins. Amber and copal are fossil resins, though the latter is also obtained direct from the trees.

Balsams. These are natural mixtures of resins and essential oils and sometimes acids. They are of different degrees of consistency and by keeping the softer kinds become harder.

Caoutchouc—India Rubber. Caoutchouc is closely allied to the terpenes. The substance of which it is mainly composed has a formula which is some multiple of C_5H_8 . The caoutchouc of commerce is obtained from some half dozen different genera of tropical plants including certain climbing plants as well as trees. If the source is a tree an incision is made in the bark and the exudation collected in earthen or tin cups. As these receptacles are filled they are emptied into larger vessels all of which are brought together at some favorable location. The rubber juice is now brought to a solid form by evaporating it from a sort of bat or shovel which is dipped into the liquid juice and held over a fire until the moisture is driven off and a layer of caoutchouc left on the bat. The thickness of the layer is repeatedly increased by alternately dipping the bat into the juice and then drying it. When the layer has reached the desirable thickness it is split up one side and removed from the form and hung up to be further dried. There are several other methods of preparing the caoutchouc from the milky juice, the object in each case being to get rid of the liquid in which the caoutchouc is suspended. The manner in which the caoutchouc is dried and the source from which it is obtained account for the different forms that come into market.

All raw caoutchouc contains albuminoid and resinous bodies and often mechanical impurities, as woody fibre, earthy matter, etc., from which it must be freed before it can

be used for manufacturing purposes. The mechanical treatment of the caoutchouc is interesting and varies with the object to which it is to be put but it cannot be described here. The best caoutchouc comes from the province of Para in Brazil and other provinces of that country. It also comes from Central America, Africa, Madagascar, Asia and some of the East India Islands.

Caoutchouc is almost equally valuable for its physical and chemical properties. Its lightness, elasticity, and impermeability to water are among its most valuable properties. Caoutchouc is insoluble in alcohol but slowly dissolves in carbon disulphide, naphtha, petroleum spirit, turpentine, and benzene—the last two being the best solvents, but the petroleum solvents are generally equally used because of cheapness. Caoutchouc is not acted upon by the alkalies or the dilute acids. It is slowly oxidized in moist air. It hardens and loses its elasticity by cold and softens and becomes sticky by heat. At about 120° C. it melts and decomposes into a black viscous mass which does not harden and is a valuable lubricant for air-tight stoppers.

Vulcanized Rubber. When caoutchouc is mixed with a small per cent of sulphur and the mixture heated to about 150° C. it undergoes a most beneficial change and is said to be vulcanized. It is thought that some of the hydrogen of the caoutchouc is replaced by the sulphur and a sulpho-compound produced. The vulcanization of the rubber is accomplished after the rubber is mechanically purified. For this purpose about ten per cent by weight of sulphur is thoroughly incorporated with the rubber and the mixture subjected to the necessary temperature. Only a fraction of the entire sulphur seems to combine with the rubber but the presence of the remainder is necessary to secure the effect. The vulcanization by heat is always accomplished after the rubber articles are made into required form. Such articles are molded into shape or the different parts cut out and

joined together by rubber cement after the sulphur has been incorporated with the rubber.

Certain other bodies besides sulphur are often added to the rubber. These are not known to act otherwise than mechanically but seem to be beneficial; they are such as zinc, lead, and iron oxides, steatite, calcium and lead carbonates.

Water-proof cloths are made by spreading the sulphured rubber in a plastic state by machinery upon the surface of the fabric. Two pieces of cloth may be made to pass through rollers with their "spread-sides" toward each other which produces water proofing of double texture. The film of rubber spread upon the cloth may be made of any desired thickness. Water-proof cloths may be vulcanized by subjecting them to the required temperature or by what is known as the cold process. In this process the spread cloth is drawn slowly through a solution of sulphur chloride in carbon disulphide during which the thin rubber sheet takes up the required sulphur and need not be subsequently heated. The cold process is not as efficient as that first described.

The effects of vulcanization are to greatly increase the elasticity of the rubber and to prevent its cohering under pressure and adhering to other bodies when warm. It is no longer affected by cold, its porosity is diminished, and it is no longer soluble in the solvents of common rubber.

The water-proofing of fabrics by solution of rubber was patented by Mackintosh in 1824. Certain garments are still named from the inventor. The vulcanization of rubber was discovered by Goodyear in 1843.

Vulcanite. With a greater proportion of sulphur (twenty to thirty-five per cent) and a still higher temperature the rubber is converted into vulcanite or ebonite. It is much harder and more rigid than rubber and is used in the manufacture of combs, rulers, discs, etc.

Rubber Tubing and Threads. Rubber tubes are made in two ways—1st, the rubber is brought to a semi-plastic condition and forced through an annular mould or die, consisting of two concentric cylinders with the necessary space between them. 2nd, By cutting rubber bands of the proper width and joining their freshly cut edges by pressure, the bands being wrapped around a mandrel of the proper size.

Rubber threads are either cut from the sheets or the semi-liquid rubber is pressed through sieve-like moulds. The first method gives the rectangular threads, the latter the round.

Gutta-percha. This substance has the same empirical formula as caoutchouc. It is like that substance obtained from exudation of certain trees. It comes mainly from the Islands of the Indian Archipelago—its name signifies the gum of the percha tree. The crude gum is procured in the same way as caoutchouc and it is subjected to about the same mechanical process to free it from impurities. It is harder and less elastic than caoutchouc. It is not attacked by alkalies or dilute acids but is acted upon by strong nitric or sulphuric acid. It is an excellent electric insulator and is extensively used as a casing in submarine telegraphy, and for the covering of electric wires. It is largely used in the manufacture of medical instruments and for many cheap ornaments.

Gutta-percha was for a long time obtained by felling the trees, the juice then exuding from incisions made at many places along the body and branches. This injudicious method was beginning to imperil the supply and has now been stopped. Because of the great demand for gutta-percha and caoutchouc, the English Government has attempted to cause the artificial production and spread of the parent trees.

ALCOHOLS.

This term is applied to a large number of bodies which in many respects differ widely from each other, but may all be considered as oxygen derivatives from the hydrocarbons. The relations of the alcohols

indicate that they may be considered as derived from the corresponding hydrocarbons by the substitution of hydroxyl (OH) for an atom of hydrogen. Thus methyl-alcohol has the composition CH_3OH which may be supposed to result by substituting (OH) for H in CH_4 ; propyl-alcohol has the composition $\text{C}_3\text{H}_5(\text{OH})_3$ which results by substituting $(\text{OH})_3$ for H_3 in propane, C_3H_8 . It is evident therefore that they may be considered as compounds of hydroxyl and hydrocarbon radicals of different degrees of valency.

Alcohols are said to be monatomic, diatomic, triatomic, etc., or monohydric, dihydric, trihydric, etc., according to the number of hydroxyl groups they contain. Each series of hydrocarbons has its derived alcohols. It will be necessary to refer to only a few of this large class of bodies.

Alcohols of the Paraffin Series. The alcohols of this series are the most important of these bodies and embrace all of those that need to be referred to here. They may be considered as derived from the paraffin hydrocarbons by the substitution of (OH) for H.

Monohydric Alcohols. The lowest members of the series of alcohols are mobile liquids, the middle members are oily liquids, and those containing twelve or more carbon atoms are solids.

There are two very important monohydric alcohols, the methyl-alcohol and the ethyl-alcohol, their formulæ being CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, the corresponding paraffins are methane (CH_4) and ethane (C_2H_6).

Methyl-Alcohol; $\text{CH}_3(\text{OH})$. This body is popularly known as wood-spirit and is found among the products which result from the destructive distillation of wood. The condensed products from distilled wood separate into lighter and heavier parts. The lighter part is the crude wood-vinegar and consists mainly of an aqueous solution of acetic or pyroligneous acid with a small proportion of methyl-alcohol. By fractional distillation the alcohol can be separated and purified. In the impure state after one distillation it is sold as wood-naphtha. Large quantities of methyl-alcohol are now made by distilling certain residues which result in the beet-root sugar factories after the fermentation of the molasses for the production of common alcohol.

Pure methyl-alcohol is very similar in smell, taste, and appearance to common alcohol. It dissolves resins and volatile oils, can be burned in lamps, and for all these pur-

poses can be used as a substitute for common alcohol. When crude it has an offensive odor and a very disagreeable taste.

Ethyl-Alcohol, Common Alcohol. This is the longest and best known of the alcohols and is generally designated simply by the term *alcohol*. It is a monohydric alcohol derived from the second member of the paraffin series, ethane (C_2H_6), by the hydroxyl substitution $C_2H_5.OH$.

Alcohol can be made artificially by the synthesis of its elements, C_2H_2 being first produced, this converted into C_2H_4 , and then converted into alcohol.

Alcohol for commercial purposes is always obtained from the fermented products of certain kinds of sugar. Fermentation is a slow process of transformation which is brought about in certain organic bodies by means of substances called "ferments." All ferments are unstable nitrogenous bodies and may be divided into two classes. 1st, Those having an organized structure and capable of growth and multiplication; 2d, Those without structure and incapable of reproduction.

The alcoholic or vinous fermentation, by which alcohol is produced from sugar, is brought about by a ferment of the first class called *yeast*, which is a vegetable micro-organism.

If to a solution of grape or cane sugar (which contains in addition the necessary elements for the growth of the yeast) a little yeast be added the process of fermentation will be set up, during which the sugar will be converted into carbon dioxide and alcohol. The precise action of the yeast is not known but it is during the growth of the yeast that the change is brought about. In the case of grape sugar or glucose ($C_6H_{12}O_6$) the molecule seems to split into carbon dioxide and alcohol, $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. Cane sugar ($C_{12}H_{22}O_{11}$) is first converted by the yeast into glucose by the assumption of a molecule of water, $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$; the glucose is then resolved as before.

NOTE.—During the fermentation other substances are produced the most important of which are glycerine, succinic acid, and fusel oil, but about 95 per cent of the sugar may be converted into alcohol and carbon dioxide.

Fermentation does not take place at a temperature below 32° F. nor above 95° F. Many chemicals arrest and prevent fermentation, such as the strong acids and antiseptics.

Pure yeast spores will not ferment a pure solution of sugar because the constituents for the growth of the yeast are absent. Water containing more than one-half its weight of sugar in solution can not be fermented by yeast and the fermentation ceases when the alcohol produced constitutes one-sixth the weight of the solution. The yeast increases greatly in weight when the necessary food constituents are present.

The sugars most generally fermented for the production of alcohol are not those from the cane and grape but those from the starch of grain and potatoes. The starch ($C_6H_{10}O_5$) is first converted into glucose ($C_6H_{12}O_6$) by the action of dilute acid or into maltose ($C_{12}H_{22}O_{11} + OH_2$) by the process of malt-ing yet to be described.

The maltose undergoes the vinous fermentation under the action of yeast just as do the other sugars mentioned.

By successive fractional distillations of the fermented solutions pure alcohol is obtained.

Pure alcohol is a colorless mobile liquid, has a pungent odor and a piercing, burning taste. Its boiling point is below that of water (78° C.) and it freezes at—130° C. It burns with a pale blue flame free from smoke. It mixes with water in all proportions and has considerable affinity for it, absorbing its vapor from the air and abstracting it from animal and vegetable substances immersed in it. This fact partly explains its action in preserving bodies. Its dilution with water results in contraction of volume and a considerable rise of temperature.

Alcohol is very valuable in the laboratory as a solvent

standing next to water in this respect. It dissolves a large number of both organic and inorganic compounds and is especially useful in dissolving the resins, essential oils, etc.

The strength of alcohol can be determined from its specific gravity and tables are prepared for this purpose. Absolute alcohol has a specific gravity of .79 at 15° C. Its strength decreases as its specific gravity increases. So-called proof-spirit has a specific gravity of .92 and contains 49 parts by weight of alcohol. If the alcoholic solution contains other bodies than water the specific gravity, of course, does not indicate the strength.

It may be observed that ethyl-alcohol is a homologue of methyl-alcohol as appears from their formulæ, CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, the two differing by CH_2 .

The acetylene, olefine, and benzene series of hydro-carbons have their mono-hydric alcohols which may be regarded as formed from these hydrocarbons in the same manner as the ordinary alcohols are formed from the paraffin series.

GLYCEROLS; TRIHYDRIC ALCOHOLS.

These alcohols may be considered as derived from the paraffin hydrocarbons by the replacement of three hydrogen atoms by three molecules of (OH). Only a few such are known. The most important of these only will be referred to.

Glycerine; Propenyl or Propyl Alcohol. The basic member of the paraffin series for this alcohol is propane (C_3H_8) in which three atoms of hydrogen have been replaced by three molecules of (OH).

Preparation of Glycerine. It has already been stated that glycerine is produced during vinous fermentation, but it is always prepared by saponifying the natural fats.

Method The natural fats are ethereal salts of the fatty, organic acids, that is, salts of the organic acids in which the typical hydrogen of the acid is replaced by the alcohol radical. The more important of the animal and vegetable fats and oils are

mainly composed of a fatty acid in which the hydrogen is replaced by the radical of propenyl-alcohol or glycerine (C_3H_5). Such fats are therefore termed glycerides and representing the fatty acid by HFt the formula for the fat or ethereal salt will be $C_3H_5Ft_3$.

When these fats are boiled with a caustic alkali there is produced a soap and an alcohol and the process is termed saponification. The reaction may be indicated thus, $C_3H_5Ft_3 + 3KOH = C_3H_5(OH)_3 + 3KFt$.

The potassium salt of the organic acid is a common soap. The term saponification is not now limited to the actual production of a soap but includes as well the processes by which ethereal compounds are resolved into an alcohol and a fatty acid.

2nd Method

Preparation of Glycerine. Glycerine is now produced by the action of super-heated steam upon fats, *saponification by super-heated steam*. The action of the steam is similar to that of the alkali and may be represented by the reaction $C_3H_5Ft_3$ (fat) $+ 3H_2O = C_3H_5(OH)_3 + 3HFt$. The chemical results of saponification are expressed in the above reactions and the subsequent preparation of glycerine is a question of purification. When pure fats or oils are saponified by steam the glycerine and the fatty acid are both obtained pure. Crude glycerine is obtained in large quantities in the preparation of soap and of the fatty acids. Glycerine has been prepared artificially.

Properties of Glycerine. Pure glycerine is a colorless viscid liquid without odor and it has a very sweet taste. It readily absorbs moisture and mixes with water in all proportions. Its boiling point is about $290^\circ C$. and it solidifies at about $40^\circ C$. It burns with a bluish flame when heated to $150^\circ C$. At high temperature it volatilizes and partially decomposes yielding acrolein (C_3H_4O), which gives the dis-

agreeable odor often observed from a partially extinguished candle.

Glycerine is a very powerful solvent, dissolving many substances more freely and some that water will not dissolve. It ranks next to water as a solvent. Glycerine is sometimes used in confectionery to sweeten and by brewers to increase frothing in beer. Because of its attraction for water it is used to prevent certain bodies from becoming dry and hard, such bodies being moist with it, as sponges when used for cushions or mattresses. Its most important use is in the manufacture of nitro-glycerine and other high explosives yet to be described.

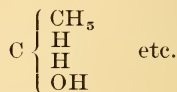
By a comparison of the formulæ of the three alcohols described, it will be seen that they constitute an homologous series of which methyl-alcohol is the first term. These formulæ will also show that ethyl- and propyl-alcohol may be considered as derived from the methyl-alcohol by the substitution of a hydrocarbon radical for an atom of hydrogen—



Methyl alcohol,



Ethyl alcohol,



Propyl alcohol.

The series might be continued to include other members of the monohydric alcohols. It will be seen by considering the formulæ that the different alcohols appear to be derived from methyl-alcohol by the substitution of hydrocarbon groups for an atom of hydrogen. An alcohol from methyl by the replacement of only one atom of hydrogen by a hydrocarbon group is a primary alcohol; all of the above are primary alcohols. If two atoms of hydrogen in methyl alcohol are replaced by hydrogen radicals the result is a secondary alcohol and if three be thus replaced it is a tertiary alcohol. The general formulæ for primary, secondary and tertiary alcohols would be represented as below in which R stands for a hydrocarbon radical.



Primary alcohol,



Secondary alcohol,



Tertiary alcohol.

The formulæ representing the constitution of the alcohols are the results of generalizing from many experimental facts and they serve admirably to explain the facts.

The oxidation of primary alcohols by which hydrogen is removed and no other change in the atomic constitution produced yields an aldehyde. The aldehydes from primary alcohols differ in constitution from the parent alcohol by two atoms of hydrogen—thus ethyl alcohol by losing two atoms of hydrogen yields acetic aldehyde (C_2H_4O). The other primary alcohols yield corresponding aldehydes. The similar oxidation of the secondary alcohols with the elimination of hydrogen yields the ketones or acetones, which are the aldehydes of the secondary alcohols.

ACETIC ACID.

This acid is a member of a group of organic acids which may be considered derivatives by oxidation of the primary alcohols or from the aldehydes of these alcohols. They are generally called fatty acids because many of them are contained in fats or derived from them.

Preparation of Acetic Acid. Acetic acid occurs among the products of the destructive distillation of wood and much acid is obtained from this source. The crude acid from wood is called pyroligneous acid and is found in the aqueous or lighter of the two layers into which the condensable products of the wood separate. The acetic acid is generally obtained from the solution by first producing an acetate by the addition of a suitable base and then decomposing the acetate by a less volatile acid. The acid liquor is generally neutralized by sodium carbonate and concentrated to crystallization by evaporation. The sodium acetate is carefully heated to expel tarry matter and distilled with sulphuric or hydrochloric acid, $NaC_2H_3O_2 + H_2SO_4 = C_2H_4O_2 + NaHSO_4$. During this operation the acetic acid passes over and is collected. An impure acetic acid may be prepared by carefully distilling the crude liquid without previous neutralization.

Alcohol may be oxidized to acetic acid by means of platinum black in a very short time. Some chemical works especially on the continent of Europe have employed this method. The power of the platinum to accomplish this oxidation is undoubtedly due to its power of condensing gases already referred to. The alcohol is placed in evaporating dishes in each of which stands a small tripod a couple of

inches high. The tripod supports a smaller dish or watch-glass in which the platinum black is contained. By a suitable temperature the alcohol is volatilized and the vapor oxidized by the oxygen condensed on the platinum. The operation is accomplished in a suitable case or chamber to which the air has to be admitted at proper intervals. The pure acid is prepared by distilling the pure sodium acetate with pure sulphuric acid.

The pure acid is a clear colorless liquid and has a pleasant but penetrating odor. It has a very sharp acid taste and when pure blisters the skin. The boiling point is 118°C . and below 170°C . it is generally solid giving glacial acetic acid. Its vapor burns with a pale blue flame. Most of its salts are soluble, hence it can not be readily precipitated.

Acetic acid is largely used in the dilute form as vinegar and in the preparation of various acetates many of which are used in the arts. The acid is an important solvent for many organic bodies and is accordingly valuable in the laboratory.

Preparation of Vinegar. Acetic acid is the acidifying principle of common vinegar. Vinegar is always made by the oxidation of alcohol and the best vinegar is made by the spontaneous acidification of wine or cider. It is only necessary to expose the wine or cider to the action of the air at a suitable temperature. The alcohol present in the liquor is gradually converted into acetic acid by oxidation, $\text{C}_2\text{H}_5\text{O} + \text{O}_2 = \text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O}$. The oxidation in this case is known to be brought about by a microscopic vegetable organism, *mycoderma aceti*, in the fermented liquor. The wine or cider contains the necessary ingredients for the growth of the organism and the oxidation of the alcohol is in some way brought about by the plant. Fermented liquors are very liable to become sour owing to this action but distilled liquors are not subject to the change since the food constituents for the organism do not exist in them.

Vinegar is also made by mixing dilute alcohol or other

distilled spirits with yeast or other nitrogenous organic matter and exposing it to the air. The added matter contains the constituents of growth necessary for the ferment and the action is the same as for fermented liquors. The conversion of the alcohol into the acetic acid may be hastened by perfecting the exposure of the spirituous liquors to the air. The *quick vinegar* process consists in causing the wine or other prepared alcoholic liquor to trickle through casks containing shavings so as to expose a large surface to the air, the shavings having been steeped in vinegar to assure the presence of the ferment.

Vinegar contains usually not over 5 per cent of acetic acid. In some countries it is permitted to add one-tenth of one per cent of sulphuric acid to the vinegar to prevent further *mothering*.

In this country a large quantity of excellent vinegar is made by the farmers from cider.

ACETATES.

Acetic acid is a monobasic acid and forms a large number of salts. Many of these acetates are employed in the arts and some of the more important will be mentioned; all of the normal acetates are soluble.

Aluminum Acetate. This salt is prepared by bringing together in solution common alum (double sulphate of aluminum and potassium) and lead acetate. Lead sulphate is precipitated and separated by filtration. The solution of aluminum acetate is largely used in dyeing and calico printing. The cloth is impregnated with a solution of the salt and subjected to a moderate heat or other process of "fixing" by which it is converted into an insoluble basic acetate in the fibre of the cloth. The fibre is then capable of taking up and *setting* permanently the coloring matter. Such bodies are called mordants and the acetates of the sesquioxides or weaker bases are the most useful, for they are most easily

converted into insoluble basic salts. The sesquioxides of aluminum and chromium form very important acetates. The solution of aluminum acetate is generally termed *red liquor* in the factories owing to the fact that it is so generally employed in fixing red colors. The red liquor may be prepared from aluminum sulphate instead of alum.

Lead Acetate. This compound is prepared by dissolving litharge in acetic acid or by acting upon sheet lead with the vapor of acetic acid. It can be obtained in distinct crystals but is usually indistinctly crystalline. It has a sweet taste and is frequently called "sugar of lead." It is very extensively used in the preparation of alum mordants and in the manufacture of certain pigments. It is a valuable article in the laboratory.

Copper Acetates. Verdigris is a mixture of several basic copper acetates and results when copper is simultaneously exposed to the action of the air and the vapor of acetic acid. It finds some use in oil and water colors, in calico printing and in the preparation of certain paints.

Sodium Acetate. Is prepared by the action of acetic acid upon sodium carbonate. The solubility of the acetate in water increases very rapidly with the increase of temperature and the supersaturated solutions have been used in foot-warmers in certain European railways. The cooling of the heated solution is greatly retarded by the heat given out by the crystallization of the salt.

SOME IMPORTANT VEGETABLE ACIDS.

Four of the more common vegetable acids are oxalic, tartaric, malic, and citric—they are all paraffin derivatives.

Oxalic Acid. This acid occurs free in certain varieties of boletus (pink or touchwood mushroom), combined with potassium in sorrel and certain plants of the rumex (dock) species and in garden rhubarb and as calcium salts in many plants.

Oxalic acid is produced on the manufacturing scale by the oxidation of highly carbonized organic bodies such as starch, sugar, and

cellulose. The principal commercial process now is by the oxidation of sawdust.

The acid can be obtained in colorless transparent crystals which are soluble in less than their own weight of hot water and in about eight parts of water at 15.5° C. The solution has a very sour taste and is very poisonous. Chalk or magnesia furnishes the best antidote.

The acid is largely used as a discharge in calico printing and dyeing, for bleaching flax and straw, for removing ink and iron stains from linen, and for cleaning metals, marble, and wood.

Oxalic acid is bibasic ($C_2H_2O_4$) and its metallic salts are in general soluble, that of calcium being least so. Calcium chloride may be used as test for a soluble oxalate.

Tartaric Acid; $C_4H_6O_6$. This term and formula include four isomeric bodies but they differ in physical properties. The ordinary tartaric acid is the acid of tamarinds, mulberries, pine-apples, grapes, and several other fruits. It occurs in the pure state in small quantity but is usually present in combination with potassium as an acid salt. The commercial supply of the acid is obtained from grape juice.

During the fermentation of grape juice in the manufacture of wine an impure acid potassium tartrate is deposited, which is known as *argol* or cream of tartar. This tartrate is dissolved and neutralized by the addition of powdered chalk or lime by which calcium tartrate is precipitated. The calcium tartrate is heated with sulphuric acid when calcium sulphate is formed and the tartaric acid left in solution, which can then be crystallized by evaporation.

Tartaric is one of the most important vegetable acids. It is largely used in the printing industries both as a "resist" and as a "discharge" and also as a mordant in dyeing wool. It is remarkable as forming a very slightly soluble acid potassium tartrate when a potassium salt in solution is added to a solution of the acid, thus serving as a preliminary test for a potassium salt in solution.

Tartaric acid forms a large number of single and double salts. Rochelle salt is a double tartrate of potassium and sodium. Tartar emetic is a double tartrate of potassium and antimony. Tartaric acid is bibasic.

Malic Acid. This acid or its salts are widely distributed in the vegetable kingdom. The acid occurs in grapes, unripe apples, blackberries, and in considerable quantity in the garden rhubarb. It is generally prepared from the unripe berries of the mountain ash.

Malic acid is bibasic and its formula is $C_4H_6O_5$.

Citric Acid. Citric acid occurs in large quantity in the juice of lemons, limes, bergamots, and is present in many other fruits and in the sap of many plants. It is prepared in the largest quantity from lemon juice. This juice is neutralized by chalk and the calcium citrate pro-

duced is decomposed by sulphuric acid. The uses of the acid are well known. Some of the citrates as those of iron and magnesium are used in medicine.

The acid is tribasic, its formula being $C_6H_8O_7$.

Tannic Acid, Tannin. This name has been given to a group of plant constituents which are capable of precipitating a solution of gelatine and of uniting with animal membrane giving a more or less perfect leather.

Gallotannic Acid. This is the best known and most important of this group and is generally called tannic acid. It is present in large quantity in gall-nuts from which it may be obtained by digesting the powdered gall-nuts in an aqueous solution of ether. Upon filtering the solution and allowing it to stand, the ether separates from the water carrying with it the coloring matter, the water containing the acid. By evaporation the gallotannic acid is left as a yellowish, friable, amorphous mass showing no tendency to crystallize. A strong solution of gallotannic acid gives a precipitate when mixed with sulphuric or hydrochloric acid. The acid precipitates albumin and gelatine.

With ferric salts the acid gives a blue-black precipitate which is the basis of certain writing inks. A tincture of nut-galls is accordingly a delicate test for the presence of ferric salts.

The tannins, extracted from the oak, hemlock and similar species and which are used for tanning leather are closely related to the gallotannic acid and are employed in tanning because of their similar action on gelatine.

ALCOHOL ETHERS.

This class of ethers may be considered as derived from the alcohols by replacing the hydrogen in the hydroxyl of the alcohol by an alcoholic radical. Thus in ethyl alcohol C_2H_5OH , if the hydrogen of the hydroxyl be replaced by the ethyl alcohol radical (C_2H_5), we shall have $C_2H_5OC_2H_5$.

We may also consider them as oxides of the alcohol radicals $\overset{C_2H_5}{\underset{C_2H_5}{O}}$, or as anhydrides of the alcohols formed by the elimination of the water from two molecules of alcohol, $2C_2H_5O - H_2O = C_4H_{10}O$.

Ethyl-ether, Common Ether. This compound can be produced by the action of several dehydrating agents upon alcohol but the process is not one of simple dehydration. Ether is made on a large scale by distilling a mixture of alcohol

and sulphuric acid. The first action when the alcohol and acid are heated together results in the formation of ethyl-sulphuric acid, $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_5\text{HSO}_4 + \text{H}_2\text{O}$. When the ethyl-sulphuric acid is heated with more alcohol, ether results and the sulphuric acid is reproduced, $\text{C}_2\text{H}_5\text{HSO}_4 + \text{C}_2\text{H}_5\text{OH} = \text{C}_4\text{H}_{10}\text{O} + \text{H}_2\text{SO}_4$.

This acid will act upon fresh alcohol and if the supply of alcohol be properly regulated and the temperature kept within proper limits the etherification process can be made continuous.

The continuous operation is effected by distilling the mixture of acid and alcohol in a retort so arranged as to admit fresh alcohol in regulated quantity so that the temperature of the mixture is kept within the required limits, about 140°C .

The ether and water distil over and are condensed in a receiver together with some alcohol and a little sulphurous acid. The sulphuric acid is gradually used up so that the process can not be continued indefinitely with the same supply of acid.

To avoid the danger of contact of the alcohol vapor with flame, coils of tubing conveying superheated steam or the vapor of some liquid of high boiling point are used as the source of heat. The distillate is shaken with water which removes most of the alcohol, a base (lime, potash or soda) is added to fix the sulphurous acid. The remaining water is removed by distilling over lime or calcium chloride. These operations may be partially repeated for greater purity.

Properties of Ether. Ether when pure is a thin, mobile, transparent and colorless liquid with fragrant odor and peculiar taste. Its specific gravity at 15°C . is .70. Its boiling point in the air is 34.9°C . Under atmospheric pressure it evaporates rapidly producing great cold. It is very combustible and its vapor very dense, which properties make careful handling necessary for safety. It mixes with alcohol in all proportions but is slightly soluble in water (one part

in ten). This fact gives a means of separating it from alcohol when the latter is not present in too large a quantity.

Ether is a solvent for resins, fats, alkaloids, and many other organic substances. It also dissolves phosphorus, iodine, and bromine. It is used to dissolve collodion cotton in photography and as an anæsthetic.

CYANOGEN AND ITS COMPOUNDS.

Cyanogen (C_2N_2), is a colorless gas with the odor of bitter almonds. It is very poisonous. Cyanogen occurs in the gases of blast furnaces and can be prepared by heating silver cyanide strongly ($AgCN$). Silver cyanide is produced when potassium cyanide and silver nitrate are brought together in solution, $KCN + AgNO_3 = KNO_3 + AgCN$. Potassium cyanide is always produced when nitrogen, charcoal, and potassium carbonate are highly heated together. Cyanogen is generally obtained by heating mercuric cyanide. In many compounds, cyanogen acts like an element. It may be regarded as a monovalent group and is generally represented by Cy .

Hydrocyanic Acid; HCN . This acid commonly known as *prussic acid* is found in the kernel of the peach and plum stones and in the leaves of the cherry and the laurel. It can be prepared by acting upon metallic cyanides with hydrochloric acid, $KCN + HCl = KCl + HCN$. It is a colorless liquid and very volatile. The inhalation of the vapor is very dangerous and the acid taken internally is one of the most fearful poisons known.

Potassium Ferrocyanide. *Yellow prussiate of potash*, $(KCN)_4$, $Fe(CN)_2 \cdot 4aq$, *double cyanide of potassium and iron*. This salt is the source of most of the cyanogen compounds and is made on the large scale by melting together potassium carbonate and iron filings or scraps, mixed with organic matter containing carbon and nitrogen. It crystallizes in large, lemon-colored crystals, readily soluble in water. This ferrocyanide is a chemical reagent of great importance and value, with a large number of metallic salts it gives precipitates which are frequently very characteristic. It is largely employed in the manufacture of colors, in dyeing and calico printing, and as stated, is the source of many of the compounds of cyanogen.

Potassium Cyanide; KCN , KCy . This substance as already stated, is produced when nitrogen is heated to a high temperature in contact with potassium carbonate and charcoal. It is also produced when potassium is heated in cyanogen gas or the vapor of hydrocyanic acid but it is generally prepared by fusing the ferrocyanide of potassium with potassium carbonate. The cyanide then generally contains some cyanate and carbonate of potassium, but for most applications this impurity is not important.

A solution of KCy dissolves the chloride and iodide of silver, in consequence of which it finds use in photography. It is used in the extraction of gold from its ores and its double cyanide with gold and silver are used in electroplating and gilding. Its great solvent powers make it useful in cleaning gold and silver.

Potassium Ferricyanide; $(\text{KCN})_3, \text{Fe}(\text{CN})_3$. This salt is often termed the red prussiate of potash. It is prepared by the oxidation of the yellow prussiate of potash. It is a powerful oxidizing agent when used with alkali; such a preparation bleaches indigo. It is used in calico printing.

Mercuric Cyanide; $\text{Hg}(\text{Cy})_2$. This cyanide is prepared by dissolving mercuric oxide in hydrocyanic acid. It is used to obtain cyanogen.

There is a large number of other cyanides, the most important of which are certain complex cyanides used as colors. Such are Prussian Blue, a complex cyanide of iron; Hachets Brown, a cyanide of iron and copper.

PHENOLS.

The phenols are benzene derivatives in which hydrogen of the benzene group is replaced by hydroxyl. They are derived from the benzene hydrocarbons in the same way that the alcohols of the fatty series are derived from the paraffins.

Phenol, Hydrobenzene, Carbohic acid, Phenic acid, $\text{C}_6\text{H}_5\text{OH}$. Phenol is found among the products resulting from the destructive distillation of wood and coal. It is usually prepared from coal tar, being the chief constituent of the acid portion of this tar. It is concentrated by collecting apart that portion of the heavy oil from coal tar which distils over between 150° and 200°C . It is extracted from the distillate.

Phenol crystallizes in colorless needles which have the odor of coal tar. It liquefies at 42°C . and is then slightly heavier than water. It is soluble in 15 parts of water at common temperature. It is poisonous, blisters the skin and exerts an antiseptic action, arresting fermentation and putrefaction. There are several disinfecting powders which consist of carbohic acid mixed with mineral matter.

CARBOHYDRATES.

This term includes three groups of bodies each of which contains six atoms of carbon or some multiple of six and oxygen and hydrogen in the proportion to form water. These groups are nearly allied to each other and widely distributed in nature.

The three groups are the *glucoses*, the *sucroses* or *saccharides*, and the *amyloses*. The first two groups constitute the sugars, the last includes the starches and the celluloses. The formula of the glucoses is $C_6H_{12}O_6$; of the sucroses $C_{12}H_{22}O_{11}$ and of the amyloses $(C_6H_{10}O_5)_n$.

The first two groups are among the most important foods of the civilized nations and the last supplies man with a large portion of both food and clothing.

Some bodies are now classed as among the carbohydrates which do not contain six atoms of carbon. The general formula of the glucoses is $C_n(H_2O)_n$ but n is not always six; of the sucroses $C_n(H_2O)_{n-1}$; of the amyloses $(C_6H_{10}O_5)_n$. Several of the sugars have been shown to be aldehyde or keytone alcohols.

Glucoses. *Ordinary glucose; Dextrose* $C_6H_{12}O_6$. Ordinary glucose is the most important member of the glucoses. It exists in the juice of sweet grapes, in raisins, and in honey of which it forms the crystalline portion. Its presence in urine is characteristic of the disease called diabetes.

Dextrose is made on a commercial scale from starch by heating it with dilute sulphuric acid. In this country it is made in enormous quantities from corn-starch, hence, is sometimes called corn-sugar. The starch is obtained from maize or Indian corn and will be referred to under the subject of starch. In other countries starch from other sources is used.

In this country the term glucose among the manufacturers is limited to the liquid products and such use of the term has become very general. The solid product is termed sugar. The manufacture of glucose in the United States is an immense industry and the products in both the solid and

liquid forms are very extensively used; many kinds of syrup are composed of the liquid glucose and the solid is largely used in confectionery and as sugar.

The conversion of the starch is accomplished by boiling it with water in large converters with from one to one and one-half per cent of sulphuric acid. The heating is often done in closed converters and under considerable pressure, steam being admitted for the purpose. The higher the pressure the shorter the time required for the conversion. For the liquid glucose less acid and less heating are required than for the sugars. During the heating the starch first passes into the isomeric dextrin and this takes up the elements of water to form dextrose, $(C_6H_{10}O_5)_n + (H_2O)_n = (C_6H_{12}O_6)_n$.

The acid is removed by the addition of powdered chalk and the liquid filtered through animal charcoal and evaporated to the desired consistency. The evaporation is frequently done in vacuum pans. The glucose can be made perfectly colorless. A little cane syrup is often added to the glucose to give the desired color. Some glucose is employed in the preparation of artificial honey, the comb being made of paraffin.

Liquid glucose obtained as above described contains considerable dextrin and maltose with some organic salts of calcium. The first two substances are less abundant in the solid glucose. Chemically pure glucose has to be obtained through further treatment.

Dextrose is less sweet and the solid forms less soluble than cane sugar.

The cellulose of wood fibre can be converted into glucose and some of the wood-paper manufacturers have attempted the commercial manufacture of glucose from this source.

Fruit Sugar; Lævulose; $C_6H_{12}O_6$. Fruit sugar nearly always accompanies dextrose in the juice of sweet fruits. It is more difficult to crystallize than dextrose. It is sweeter than dextrose and less easy to ferment. A mixture of dextrose and lævulose in equal proportions constitutes "invert" sugar.

SUCROSES.

Common Sucrose; Cane Sugar; $C_{12}H_{22}O_{11}$. Cane sugar is the most important member of this group. It is very widely distributed in the vegetable kingdom but is obtained on a commercial scale from only a few plants. The principal of these are the beet-root, sugar cane, sorghum, sugar maple, and a species of palm. A small amount is made in this country from the ash-leaved maple or box-elder and from melons.

More sugar is now derived from beets than from any other single source.

The manufacture of cane sugar is an important industry of many countries and only the general principles involved in the operations can here be referred to.

From the cane the juice is extracted by crushing between rollers. Lime is added to the juice to prevent the inversion of the sugar. It is also generally subjected to the action of sulphurous acid to prevent fermentation. The juice is then heated to coagulate albuminous matter, which rises to the surface as a scum. The liquid is then separated from the scum and sediment, and evaporated to the crystallizing point. It is then allowed to cool and crystallize and the molasses drained off. This product is the raw sugar and has to be still further treated to obtain refined sugar. The refining is accomplished by re-resolution in hot water, filtration, and decolorization by passage through animal charcoal and evaporation in vacuum pans. The steps in the preparation of beet sugar are essentially the same as in cane sugar but the juice of the beet is generally extracted by the "diffusion" process and not by mascerating the beets and pressing the pulp. For diffusion the beets are cut into thin slices and subjected to the action of warm water by which the juice is effectually extracted. The diffusion process has also been applied to the cane.

Nearly all the beet sugar is made in Continental Europe.

The cane sugar is derived from many localities, but mainly from Cuba, Java, Manila, Brazil, Mauritius, and Louisiana.

Properties of Sugar. Many of the properties of sugar are too well known to mention. It melts at 160°C . and forms an amorphous mass upon cooling. If kept at that temperature for some time it is converted without loss of weight into dextrose and an uncrystallizable syrup, lævulosan ($\text{C}_6\text{H}_{10}\text{O}_5$). At a higher temperature it loses water and becomes brown, yielding according to Bloxam, "caramelan" ($\text{C}_{12}\text{H}_{18}\text{O}_9$). Caramel is composed of this body mixed with other substances and is the result of the action of heat upon sugar. Caramel is largely used to color alcoholic liquors.

Maltose; $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. This body results from the action of malt upon starch. The germinating grain (malt) contains a peculiar substance "diastase" which causes the starch to undergo hydrolysis, forming maltose and dextrose. Crystallized out of alcoholic solution maltose has the same composition as cane sugar, but from aqueous solution its formula is $\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{H}_2\text{O}$. It becomes anhydrous at the boiling point of water.

Amyloses, Starch and Cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$)_n. The best known and the most important members of the amylose group are starch and cellulose.

Starch ($\text{C}_6\text{H}_{10}\text{O}_5$)_n. This is one of the most widely diffused bodies of the organic kingdom. It occurs in all plants that have been examined except certain fungi and abundantly in the seeds of plants, especially of those cereals used for food. Rice, wheat, and Indian corn contain it in largest proportions.

Fully two-thirds or more of the food of mankind is derived from the carbohydrate group and starch furnishes much the largest proportion.

Starch is necessary to the growth of plants and its presence in the seeds affords nourishment to the young sprouts.

Preparation of Starch. In the United States starch is generally prepared from maize (Indian corn); in England from rice and potatoes; on the continent of Europe from

potatoes and wheat. The object in each case is of course to separate the starch from the other constituents. The outline of the method adopted in this country will give an idea of the principles involved in all cases.

The cleaned grain (maize) is steeped in water for about 30 hours until soft enough to grind. It is then crushed by rollers or ground between millstones and washed upon sieves. The pulpy mass left upon sieves may be reground and subjected to a second washing. The milky liquid carrying the starch flows into or over inclined boxes known as *starch-tables* during which time the starch granules are deposited. The liquid passing on from the starch-tables flows into tanks in which are deposited certain nitrogenous matter. This latter is mixed with the husks from the sieves and worked up for cow and pig-feed.

For further increasing the purity of the starch by the removal of the nitrogenous matter it is washed in a dilute solution of alkali (caustic soda) and again allowed to settle, the escaping liquid carrying off the nitrogenous matter, oils, etc. The starch is again thoroughly washed to remove alkali. The several subsequent operations are mechanical. The reports from some of the large American factories show a yield of starch equal to one-half the weight of the maize employed. This indicates a heavy loss of the total starch contained. Single factories convert from five to twenty thousand bushels of corn daily.

The starch from the potato may be obtained by steeping, crushing, and washing without the use of alkali. Rice contains the greatest percentage of starch but the use of alkali is necessary to separate it from the other constituents of the grain. In the manufacture of starch-sugar or dextrose already referred to, the first step in the preparation of starch is that above described.

The finest qualities of starch are used for food, for making sugars and syrups, for sizing the finest papers, and for

laundrying. The other varieties are largely used in the industrial arts, for weavers' dressing, for thickening mordants, etc. Besides the edible starches obtained from rice, potatoes, maize, and wheat, there are several other forms.

Arrow-root. The starch known under this name is obtained from the root of several kinds of plants widely disseminated in the tropics. The most important of these flourish in tropical America from Mexico to Brazil and in the West Indies. They belong to the genus *Maranta*. The Brazilian arrow-root is frequently called cassava-starch.

Tapioca. This is a specially prepared form of the Cassava starch, other starches are obtained from the roots of various plants in widely separated places, Africa, Australia, East Indies, and China.

Sago. This is starch obtained from the pith of certain varieties of the palm, indigenous to the East Indian archipelago and the adjacent regions. These last named starches differ materially from the grain starches in that they are more nearly pure starch, more readily gelatinize, and are thought to be more easily assimilated by the human system.

Characteristics of Starch. To the naked eye starch appears as a white glistening powder but under the microscope it is seen to have an organized structure, to consist of granules generally ovoid, which are composed of concentric layers. The starch granules from different sources differ in appearance. The granules vary very much in size, those from the potato being 1-300 of an inch in the longest diameter while those from certain plants, as cactus, are not over 1-10000 of an inch. Starch is without odor, is insoluble in cold water and consequently without taste. The granules consist of starch-cellulose or farinose in the outer layers, the exterior layer being probably wholly composed of it. This cellulose is insoluble in cold water. The interior of the granules is partially soluble in cold water and is called granulose. The

insolubility of the outer layer prevents the action of cold water upon starch. When a mixture of starch and water is heated to about 70°C . the granules burst, the granulose is dissolved to a viscous liquid slightly opalescent, due to the undissolved cellulose. The solution becomes gelatinous on cooling and gum like when dried. Iodine colors starch intensely blue and the action takes place upon the granules intact as well as upon the paste. Starch heated for some time up to about 200°C . is partially converted into dextrin. The conversion into the soluble form is important in the preparation of foods.

Dextrin; $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. This body has the same formula as starch. It may be prepared by heating starch with dilute acids or by heating dried starch to a high temperature. Dextrin is soluble in water. There are several modifications of dextrin which are used as substitutes for gum.

Gums. These are amorphous bodies occurring in many plants. They are insoluble in alcohol but are soluble in water and form a viscous mass with it. Those which form a clear solution with water are real gums; the others vegetable mucilages.

Cellulose $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. This substance is the principal ingredient in the framework of plants. It constitutes the walls of plant-cells and forms a large proportion of the solid parts of all vegetables. Woody-tissue consists of the membranous cells together with encrusting material. When all encrusting material has been removed by solvents the cellulose is left.

Fine linen and cotton are composed of nearly pure cellulose, the treatment to which the fibre is subjected having removed nearly all the other material.

Pure cellulose is insoluble in nearly all ordinary solvents, is tasteless, and for a long time was thought to be absolutely innutritious, but this point is now thought to be doubtful. It is known to constitute a large part of the food of beavers. Cellulose is soluble in an ammoniacal solution of cupric

hydroxide (Schweitzer's reagent.) Cellulose is not colored by iodine.

If unsized paper be steeped for a few seconds in a mixture of strong sulphuric acid and half its volume of water, and then washed with water and dilute ammonia it is converted into a sort of parchment. It has the same composition as cellulose and is called vegetable parchment. It is translucent, much stronger than paper, is very useful in diffusion, and is largely used for baggage labels. It is not easily torn and withstands rain.

Strong sulphuric acid converts dry cellulose into a gummy mass, which by the proper manipulation may be converted into dextrose and then into alcohol; linen rags may thus be converted into alcohol.

VEGETABLE COLORS.

The vegetable kingdom exhibits great beauty and variety of color but the compositions of the coloring principles have been determined in only a few cases and only a few of the colors obtained directly from plants find application in the arts.

The most universally distributed color in nature is that of green and is due to the presence of chlorophyl which occurs in all the green parts of plants. Its composition is not known though iron is supposed to be a constituent of it. Wax and other substances are associated with it forming chlorophyl granules.

The blue coloring matter present in certain flowers has been called cyanin. It is made red by acids, consequently blue flowers can not contain acid juices, while red flowers do. Bloxam attributes the color of certain grapes and red wine to cyanin.

Saffron, Turmeric, Madder, and Litmus are all vegetable colors. The litmus is obtained from certain varieties of lichens. It is made blue by alkalies and red by acids the original color being a purplish red.

Lac is a red coloring matter extracted from a resin of the same name obtained from a tropical plant.

Carmine is a red dye obtained from the cochineal, the dried body of a species of insect which feeds upon a certain variety of cactus.

Indigo. This is obtained from the indigo plant growing chiefly in India, but also in China, Egypt, and South America. It has been known as a dye for many hundreds of years. It does not exist ready formed in the plant but is the product of the alteration of the substance

known as *indican* which is nearly colorless. The indigo is obtained by macerating the plants in water and allowing them to ferment. The indican is converted first into white indigo and then by oxidation into the common or blue indigo.

The above named dyes are all composed of carbon, hydrogen, and oxygen except indigo which in addition contains nitrogen. Indigo is extensively employed for dyeing woollen fabrics.

ALBUMINOUS SUBSTANCES.

This term includes a number of complex bodies found in vegetable and animal organisms all of which in addition to carbon, hydrogen, and oxygen contain nitrogen and most of them sulphur. Not much is known in regard to the constitution of these bodies, their molecular formulæ not having been determined. The percentage numbers indicate great conformity in chemical composition and the same conformity is shown in their general properties. The proportion of the nitrogen to the carbon, hydrogen, and oxygen is much higher than is usual in organic bodies.

The albuminous substances are sometimes divided into two classes—*albuminoids* and *proteids*. The second more closely resemble common egg-albumin and are generally coagulated by heat, the first like bone-cartilage, yield gelatine with boiling water and are sometimes termed simply gelatinous bodies. Again both classes are sometimes included under the term *proteids*.

Only a few of the most typical and common of the albuminous substances will be mentioned here.

Gelatine, Glutin. When the skin, tendons, and organic matter of the bones of the animal body are subjected to the long continued action of boiling water a solution is obtained which on cooling solidifies to a tremulous transparent mass which becomes hard and brittle on drying.

Cold water softens but does not dissolve gelatine. It is dissolved in hot water and the solution gelatinizes on cooling.

Tannin precipitates gelatine from its solution. The tissues which yield gelatine unite with tannic acid forming an insoluble non-putrescible compound, or leather.

Isinglass is a pure form of gelatine obtained from the bladder of the sturgeon and other fish.

Glue and *size* are impure gelatines made usually from the parings of hides.

Gelatine is largely used in food preparations, for clarifying wines, and in photography. Gelatine is sometimes called glutin.

A gelatinous body closely resembling the animal gelatine is also obtained from silk.

Albumins. There are several varieties of albumin differing but slightly from each other. These bodies are found in the blood, muscles,

nerves, and other organs of animals and also in nearly all parts of plants, especially the seed. It is thought that probably these bodies are synthesized by the plant and that they are taken up and appropriated by the animal with but slight change.

Egg-albumin. This exists in aqueous solution in the egg and is one of the most common varieties of albumin. It is coagulated and rendered insoluble in water by heat. Alcohol and ether also precipitate it from solution. The raw albumin of the egg does not affect silver but this metal is tarnished by cooked eggs, which also give a faint odor of sulphuretted hydrogen, indicating some decomposition in the cooking by which H_2S is liberated.

Serum-albumin. This is abundantly present in the blood and other animal secretions. It closely resembles egg-albumin but is not precipitated by ether.

Plant-albumin. This occurs in nearly all vegetable juices, it is coagulated by heat and closely resembles the egg and serum albumins.

Myosin. This is the albuminous substance present in solution in the sheaths of muscular fibres. Its spontaneous separation from the plasma after death produces the *rigor mortis*.

Fibrin. Blood fibrin is the albuminous substance which separates from the blood during coagulation or clotting. It appears to be formed from soluble albumin in the blood, by a change which is set up when the blood is removed from the vital influences. The clot is red, due to the entanglement of the red corpuscles in the fibrin. By washing, the fibrin may be separated into elastic filaments which become hard and brittle upon drying.

Vegetable Fibrin. This occurs in the undissolved state in plants and especially in the cereal grains. When wheaten flour is kneaded upon a cloth with water the soluble albumin and starch are separated and a tenaceous mass remains which is called gluten. When this gluten is boiled with dilute alcohol a portion is left undissolved and is called vegetable or plant fibrin.

Milk Casein. Casein occurs in the milk of all mammalia, most plentifully in that of the carnivora. It is the chief constituent of the curd of milk. It exists in solution in the milk due to the presence of a little alkali. If the alkali be neutralized by the souring of the milk or the addition of a little acid the casein is separated. The most striking property of the casein is its coagulability by *rennet*, the mucous membrane of the calf's stomach. Casein does not coagulate spontaneously by heat.

Vegetable Casein; Legumin. This substance is found most abundantly in the seeds of leguminous plants as beans and peas. It closely resembles animal casein and its solution is coagulated by rennet.

Gluten. It is stated above that gluten is the name given to the tenacious mass left when wheaten flour is kneaded upon a cloth with water. When treated with boiling dilute alcohol a portion of the gluten is left undissolved and is called vegetable fibrin. As the alcoholic solution cools, a white flocculent precipitate is deposited which closely resembles the casein of milk, it is called *mucedin*. On adding water to the cooled solution a third substance is precipitated, which closely resembles serum albumin and is called gluten or gliadin.

It is pertinent to recall here the fact that the albuminous substances of the animal organisms have their counterparts in the vegetable kingdom.

ALKALOIDS.

This name is given to a large class of nitrogenous vegetable compounds of a basic character. Many of them are of great medicinal importance because of the powerful action they exert on the animal system. They all contain carbon, hydrogen, and nitrogen, and nearly all contain oxygen in addition. They are soluble in alcohol and generally have a bitter taste.

Caffeine; Theine. This is the principal alkaloid of tea and coffee in which it is thought to be present as a salt of some variety of tannic acid. Tea also contains a small quantity of some other alkaloids. Caffeine is composed of carbon, hydrogen, oxygen, and nitrogen.

The fragrance which distinguishes prepared coffee does not belong to the raw berry but is developed by the roasting. In the same way the aroma of the tea is developed by heat during the drying of the leaves. Each is due to a volatile aromatic oil produced by the heat.

Nicotine. This is one of the alkaloids that does not contain oxygen. It exists as a salt of malic acid in the leaves and seed of tobacco. It is a volatile oily liquid. Nicotine and its salts are powerful poisons. Tobacco may contain from one to eight per cent of nicotine but seldom over four. Tobacco contains an unusual percentage of mineral salts. This explains the large amount of ash it leaves upon burning. This ash may amount to one-fifth the weight of the dried leaf. The salts are mainly the malate, citrate, and nitrate of potassium. The presence of these salts, especially the last, explains the smouldering combustion which these leaves undergo.

Opium. This is the thick juice which is obtained from the capsules of the opium-poppy (*popaver somniferum*). It is a complex substance containing a large number of bases, one of the most abundant and best known of these is morphine.

Morphine. This is obtained from opium in which it is present often to the extent of ten per cent. It is a white powder, soluble in 500 parts of water and has a bitter taste. Its formula ($C_{17}H_{19}NO_3$) shows it to

contain carbon, hydrogen, oxygen, and nitrogen and representing it by "M," the common medicinal form of morphine is MHCl , the hydrochloride of morphine or the muriate of morphia.

The alkaloid present in opium in most abundance next to morphine is narcotine.

Quinine. The bark of several species of the cinchona order contain a number of alkaloids usually associated with some vegetable acids. The best known of these is quinine and this is the most important of the alkaloids. It is immensely used as a febrifuge. It is found most abundantly in the yellow cinchona or Peruvian bark.

Quinine crystallizes in small crystals and to the naked eye appears as a white powder. It requires about 2000 parts of water to dissolve it and its solution is alkaline and bitter. Its composition is indicated by the formula $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$. The form of quinine generally used in medicine is the basic sulphate, which may be represented by $\text{Q}_2\text{H}_2\text{SO}_4$, Aq. in which Q stands for the formula above given.

The cinchona barks were introduced into Europe from Peru in the first half of the seventeenth century by the wife of the viceroy of Peru, the countess of Chincon from whom they received their name. The cinchonas are indigenous to the slopes of the Andes between 7° N. and 20° S. The barks richest in alkaloids grow at an altitude between 6000 and 12000 feet above the sea. The most highly prized cinchonas have been successfully cultivated in Java for nearly fifty years.

Strychnine. This is obtained from the seeds and bark of the nux vomica, from St. Ignatius' bean, and from other tropical plants. It is slightly soluble in water, is bitter, and fearfully poisonous. It is said that it can be detected by its taste when it is dissolved in a million parts of water.

Cocaine. This is obtained from the leaves of certain varieties of coca. Cocaine, in aqueous solution, is employed as a local anaesthetic and finds extended use in minor surgical applications. In small doses it acts as a stimulant and is one of the most insinuating of the poisonous drugs. The medicinal form most generally employed is the hydrochloride, BHCl .

IMPORTANT INDUSTRIAL APPLICATIONS OF CHEMISTRY.

CALORIFIC VALUE OR POWER.

The calorific power of a substance is the amount of heat evolved due to its combustion. The calorific value of the ordinary hydrocarbon fuels may be approximately calculated from their compositions. Many of these fuels contain oxygen and it is assumed that the heat developed by the perfect combustion of the fuel is equal to that due to the perfect combustion of the carbon and so much of the hydrogen as is in excess of that necessary to form water with the oxygen present. In other words it is assumed that the oxygen present is combined with hydrogen in the form of water and that the oxidized hydrogen adds nothing to the heating power. This form of computation is illustrated below.

Example.—Required the calorific value of 75 pounds of wood.

Molecular formula of wood is taken as $C_6H_9O_4 = C_6H(H_2O)_4$, molecular weight=145.

In 145 pounds of wood there are $\left\{ \begin{array}{l} 72 \text{ pounds of C; 1 pound of C produces} \\ \quad \quad \quad 8080 \text{ units of heat.} \\ 1 \text{ pound of H; 1 pound of H produces} \\ \quad \quad \quad 3442 \text{ units of heat.} \\ 72 \text{ pounds of H}_2\text{O.} \end{array} \right.$

Units of heat produced by the carbon in burning= $72 \times 8080 = 581760$.

Units of heat produced by the hydrogen in burning= $1 \times 3442 = 3442$.

Total heat produced by the 145 pounds of wood= 616222 .

Hence the calorific value of 75 pounds of wood= $\frac{616222}{145} \times 75 = 318735$.

CALORIFIC INTENSITY.

Calorific intensity may be defined as the temperature to which the heat generated by the burning fuel could raise the products of its own combustion. In the case of pure carbon, burning to carbon dioxide, the calorific intensity may be obtained from the following formula: $T = \frac{C}{WS}$, in which T is the calorific intensity, C the calorific value, W the weight of the carbon dioxide produced, and S the specific heat of the carbon dioxide. In the above formula it is assumed that the specific heat of carbon dioxide is constant at all temperatures. In such computations it should be remembered that the specific heat of gases is less at constant volume than at constant pressure so that calorific intensities would be greater at constant volume.

In the case of fuels containing hydrogen or hydrogen and oxygen in addition to carbon, there are certain considerations that do not enter the problem just given. In determining the calorific power of hydrogen the vapor of water resulting from its combustion was condensed in the calorimeter and the heat which was latent in the vapor became sensible and was properly included in the calorific value, but when the vapor is no longer condensed this heat can not be considered in the production of temperature and must be deducted from the calorific value in the formula for calorific intensity.

In fuels containing oxygen the oxidized hydrogen existing or supposed to exist as water is vaporized by part of the heat of combustion. This number of heat units must also be deducted from the calorific value of the fuel in the formula for intensity.

NOTE. In addition to these deductions there is another slight deduction which should be made from the calorific value. In the computation of the temperature produced, the initial temperature is 0°C .; between this point and the boiling point the specific heat of water is greater than that of steam in the proportion (approximately) of one to five-tenths, so that for each pound of steam produced there should be further deducted $100 \times .5 = 50$ units of heat.

The formula for the calorific intensity of fuel, like wood, containing hydrogen, carbon, and oxygen, is

$$T = \frac{C - (B)}{WS + W_v S_v + \text{etc.}}$$

in which T is the calorific intensity, C the calorific value, B the latent heat of steam produced, which comes partly from the combustion of the free hydrogen in the fuel, partly from the combined oxygen present as water and in part composing the fuel; W and W_v , are the weights respectively of the carbon dioxide and the water vapor produced; S and S_v , are the specific heats respectively of the carbon dioxide and the water vapor.

EXAMPLE.—Required the calorific intensity of wood burned in a full supply of oxygen. When burning in full supply of oxygen, $C + O_2 = CO_2$ and $H_2 + O = H_2O$; atomic weights of carbon, hydrogen, and oxygen are 12, 1, and 16, hence 12 parts by weight of carbon require 32 parts by weight of oxygen and produce 44 parts by weight of carbon dioxide; 2 parts of hydrogen require 16 parts by weight of oxygen and produce 18 parts by weight of water, hence 1 part of carbon produces $3\frac{3}{8}$ parts of carbon dioxide and one part of hydrogen produces 9 parts of water. It has been seen by the formula, that in 145 parts of wood, by weight there are 72 parts of carbon, 1 part of hydrogen, and 72 parts of water.

By combustion the one part of hydrogen produces nine parts of water, this with the seventy-two parts of water in the wood gives eighty-one parts of water to be evaporated, the latent heat of which is $81 \times 537 = 43497$.

The 72 parts of C in the wood produce 264 parts of carbon dioxide.

The specific heats are approximately $\begin{cases} CO_2 = .22 \\ H_2O \text{ (vapor)} = .5. \end{cases}$

The calorific value of 145 pounds of wood as determined above is 616222.

The heat rendered latent by the evaporation of 81 parts of

water = 43497

Heat units available for heating products of combustion... = 572725

Number of heat units to raise the products of combustion from 145 pounds of wood $1^\circ C. = 264 \times .22 + 81 \times .5$, hence the calorific intensity of wood is $\frac{572725}{264 \times .22 + 81 \times .50} = 5809^\circ +$.

The calorific intensity is independent of the weight of the body burned but is dependent upon the time and the atmosphere in which

the combustion takes place, being greatest in oxygen. If the combustion takes place in the air which is usually the case, the calorific intensity is lowered because of the large amount of nitrogen which has to be heated. The complete combustion of carbon requires $2\frac{1}{2}$ times its weight of oxygen and hydrogen requires 8 times its weight of oxygen. In the above example of wood the 72 parts of carbon will require 192 parts of oxygen and the 1 part of hydrogen would require 8 parts of oxygen, making necessary 200 parts of oxygen. Taking the formula of the atmosphere as $4N+O$, we see that for 16 parts by weight of oxygen there are present 56 parts of nitrogen or $3\frac{1}{2}$ parts of nitrogen for one of oxygen. We have seen that 145 parts of wood would require 200 parts of oxygen for combustion; in supplying this oxygen by means of the atmosphere there would be introduced $3\frac{1}{2}$ times as much nitrogen or 700 parts of nitrogen. The specific heat of nitrogen is about .25. The formula for the calorific intensity in the air would be

$$T = \frac{572725}{264 \times .22 + 81 \times .5 + 700 \times .25} = 2093^{\circ} \text{ C.}$$

In all ordinary furnaces in order to maintain the draught, much more air has to be introduced than would be required to supply the necessary oxygen. This extra amount of air still further reduces the intensity. In addition to this extra amount of air, all the heat can not be applied to heating the products of combustion as assumed in the discussion. Part of the heat is lost by radiation and some is lost in heating the grate and other parts of the furnace and in heating the unburned fuel. Again complete combustion does not always take place. From these considerations it is evident that the computed calorific intensity is only approximate.

GLASS MAKING.

The manufacture of glass is a very ancient industry, the earliest examples being of Egyptian origin. A lion's head of glass found at Thebes and now in the British Museum bears an inscription which places its date at 2400 B.C. In the tombs of Beni Hassan dating at least 2000 B.C. the process of glass blowing is represented. These two facts prove that glass was made more than four thousand years ago.

Glass is a mixture of several insoluble silicates and is destitute of crystalline structure when not too slowly cooled. One of the silicates present is always that of an alkali metal, potassium or sodium, and with these are associated one or more of the silicates of calcium, barium, lead, iron or zinc.

The mixtures of these silicates display properties that are not possessed by the single silicates. The presence of alkaline silicates is necessary in the glass, for these silicates when fused dissolve silica readily, fuse more easily than any other class, and exhibit less tendency to crystallize on cooling. The silicates of the other metals named are more infusible and less readily acted upon. By mixing the silicates in the proper proportions the requisite properties are obtained in the glass.

The most valuable and important properties of glass are its transparency, its plasticity before complete fusion, and its permanency. There are a great many kinds of glass differing more or less distinctly from each other depending upon the proportions of the constituents. The two most important divisions may be based upon the silicates present.

First, The glass which contains alkaline and calcium silicates, and second, that which contains alkaline and lead silicates. To the first class belong the common window glass, plate glass, and crown glass; to the second belong the flint or crystal glass and the material of artificial gems.

Common window glass is composed essentially of sodium and calcium silicates and is made by fusing together the proper proportions of sand, calcium carbonate, and sodium carbonate. It usually contains a little aluminum silicate owing to lack of purity in the materials employed.

Plate glass has essentially the same composition as window glass but is made from purer materials. Usually some potassium carbonate replaces some of the sodium as an ingredient.

Crown glass is composed of the silicates of potassium and calcium and is made by fusing together the proper proportions of sand, potassium carbonate, and calcium carbonate. Potassium is less likely to impart color to the glass than sodium. This glass is generally employed for optical purposes.

Bohemian glass contains the same constituents as crown glass but has a larger proportion of silica to which is due its greater permanency and infusibility.

Lead or Flint Glass. This glass is made by fusing together in proper proportions silica, lead oxide, and potassium carbonate. The oxide of lead generally used is the Pb_3O_4 . The higher oxide is preferred because the excess of oxygen serves to oxidize any organic impurities that might accidentally be present.

Colored glass is made by fusing certain metallic oxides with the ingredients of any of the above-named glasses.

The glass from which bottles are generally made has essentially the same composition as common window glass though containing less sodium and in addition some iron silicate to which its color is due.

The red oxide of copper gives a red color to glass; cobalt oxide a blue color; oxide of manganese an amethyst color.

Production of Glass. The principle of glass manufacture is simple. The materials of the glass are fused together and the silica combines with the metallic oxides forming silicates.

The fusing was formerly accomplished in large pots or crucibles of refractory fire-clay. The pots varied in size from three to five feet high and two to four feet in diameter. A number of these pots were accommodated in a single furnace and heated by gaseous fuel which played around the pots. With lead-glass covered pots were required to prevent the reduction of the lead to the metallic state by the gases of the fuel, in other cases the pots were open.

In the past dozen years the pot furnaces have been largely replaced by the open-hearth or tank furnaces, this is especially so in the manufacture of bottles and of window glass. Some of these modern furnaces are of astounding dimensions being from sixty to seventy-five feet long, from four to six feet deep and from ten to twelve feet wide, and

capable of containing over four hundred tons of melted glass.

The fused constituents of the glass are converted into a great variety of finished products by processes which differ depending upon the kinds of products desired. In general after the constituents are fused together the manufacturing operations may be grouped into four.

1st, *Crown and Sheet Glass*. A hollow glass sphere is obtained by blowing and this for crown glass is converted into a flat disc by rapid rotation. For sheet glass the globe is opened and extended into a cylinder, then split longitudinally, spread into a sheet, and flattened by suitable tools. Window glass is generally made in this way.

2nd. *Plate glass* by pouring the fused glass upon a flat table and subsequently grinding and polishing it.

3rd. *Hollow Ware*. Under this are classed all kinds of bottles as well as the more delicate glasses, vases, etc. Bottles are always made by blowing the glass into moulds, both the external and internal portions of the bottle assuming the shape of the mould. The process is a very rapid one; a "set" of five men generally work together in moulding bottles and they usually average two or three finished bottles per minute.

Wine-glasses, vases, pitchers, etc., are made by blowing and hand manipulation but little use being made of patterns or moulds. Such ware requires the greatest manual skill and can only be fashioned by the most expert workmen.

4th. *Pressed Glass*. Many kinds of glass-ware for domestic purposes are now made by moulding into shape by pressure. The external form is given by the mould and the internal by the shape of the plunger. This process has brought into use a very cheap ware suitable for nearly all domestic purposes. The lead glass was found most suitable for pressed ware but to diminish cost the lead oxide has been

replaced by barium carbonate which gives a clear glass suitable for this manufacture.

All finished glass products require to be annealed to avoid spontaneous fracture.

By using a certain kind of glass called *strass* as a base all the precious stones can be imitated except opal. The production of artificial gems is an important feature of glass manufacture.

Devitrified Glass. Certain kinds of glass containing but little alkaline silicate may be made to partially crystallize by heating nearly to the fusing point and then cooling slowly. It thus becomes opaque and is sometimes called Réaumur's porcelain. It may be made transparent by refusion.

Soluble Glass. If silica be fused with an excess of sodium or potassium carbonate it forms a glass which is soluble in water—a solution of which is sometimes used in making artificial stone. If sand be moistened with it and pressed into shape and heated highly, the glass fuses and binds the whole together. It is also used to preserve natural stone from decay, in mural painting, and in rendering wood non-inflammable.

The glass industries of the United States are mainly centered in New York, New Jersey, and Pennsylvania. The abundance of suitable sand in this country affords marked advantages for this industry. Nearly all the sand employed in glass making is mined as sand-stone and this is crushed preparatory to use. The sands of the United States suitable for making the finest grades of glass are abundant and found in many of the states. Among the beds most extensively worked are those of Berkshire County, Mass., Juniata County, Penn., Morgan County, W. Va., and some in Illinois and Missouri.

MANUFACTURE OF POTTERY.

Pottery in its widest sense includes all articles in which clay is the main ingredient and which have been hardened by the application of heat, natural or artificial. The chemical principles involved in the manufacture of a few important kinds will be given.

The properties of clay which make it the basis of all forms of pottery are its plasticity when moist which enables it to be kneaded, and its subsequent hardness when heated.

The two most general divisions of pottery are the *glazed* and the *unglazed* forms, of the first, porcelain may be taken as the most characteristic variety and highest type. Porcelain is made from the purest clay or kaolin, but a vessel made from clay alone would shrink and lose its shape in drying and be liable to crack in the kiln. To prevent this, other substances are mixed with the clay of the ware which cause it to retain its form and which fuse at the temperature of the furnace and bind the whole into a homogeneous compact mass. These fluxing ingredients differ at different manufactories and to these differences are due the various kinds of porcelain.

In the celebrated Sèvres porcelain there is added to the kaolin, feldspar and a little chalk. In the Meissen porcelain there is added feldspar and ground waste, porcelain. The other fluxes most commonly used in porcelain are sand, bone-ash, and gypsum. In each case the clay and other materials are brought to the finest state of subdivision and usually held suspended in water. The creamy liquids are then mixed in the proper proportions, allowed to settle, separated from the water, and the paste thoroughly kneaded. The proper proportions of the ingredients may be brought together in the dry state and the whole agitated together in water. In any case after the mixed ingredients are separated from the water the mass is usually left to stand for considerable time which improves the quality of the clay. This result is believed to be brought about by the oxidation of any organic matter present and to physical change brought about by drying and shrinkage which affect the plasticity of the clay. When ready for the workman the clay is moulded into the required shape by various forms of potters' wheels, jiggers and lathes, but principally by moulds. The most perfect specimens are always finished by hand.

The moulded articles are dried by exposure to the air, then packed in cases or *saggers* and subjected to a comparatively low heat of the kiln. The articles are thus sufficiently heated, dried, and hardened to receive the glaze without danger of breaking. The glaze for the porcelain must be similar to the material added for fluxing the clay. The glaze for the Sèvres porcelain is ground feldspar and quartz, for the Meissen ware it is clay, silica, and ground ware. The glaze material is very finely ground and evenly applied to the surface of the ware by dusting, ~~but~~^{or} more generally the glaze is suspended in water and the article is deftly dipped in the water and removed. Enough of the material of the glaze adheres to the surface of the ware. The ware is now completely hardened and the glaze fixed by exposure for many hours to a high temperature; the ware for this purpose is packed in *saggers* as during the preliminary heating.

The Sèvres and Meissen ware come under the head of *hard* porcelain. Hard porcelain has several characteristics which distinguish it from other forms of glazed ware. The glaze is thin and graduates imperceptibly into the body of the ware; the ware is translucent and breaks with a conchoidal fracture. Hard porcelain is unique in that the ware is subjected to but one burning, the ware being hardened and the glaze fixed at the same time.

With all other forms of glazed ware there are two "firings," one known as the biscuit firing which hardens the ware and the other fixes the glaze upon it. Statue porcelain is a true hard porcelain but is not glazed.

English *soft porcelain* is more fusible than the hard porcelain and the glazing requires a separate "firing."

STONEWARE.

This is a coarse kind of porcelain made from impure material. For glazing, the ware is coated with fine sand by dipping it in water holding the impalpable sand in suspension. During the firing of the ware damp salt is thrown

into the kiln. Decomposition ensues by which hydrochloric acid and sodium oxide are formed, the latter combines with the silica and forms sodium silicate which fuses and constitutes the glaze.

Decorating Porcelain. A uniform color can be given to the ware by mixing the proper mineral pigment with the glaze. Colors in pattern and design are put upon the ware after glazing and fixed by another firing by which the pigment is fused and firmly fixed upon the ware.

The most expensive and finest decorating is done by hand, but the design is usually engraved on a copper plate and a print taken from it in mineral colors on a sheet of tissue paper. By gentle pressure the print adheres to the ware and after a short time the paper can be removed, the firing then fixes the design.

The above general description of glazed ware applies usually to that of all countries, but only on the continent of Europe is made the hard porcelain by a single firing. In this country the white wares suitable for household purposes may be fitly placed in four grades. The finest is a true porcelain having a vitreous translucent body and a perfect accordance between glaze and ware.

Pottery kilns are solidly built circular structures of masonry rising to a crown inside and surmounted by a shaft or dome to secure draught. Around the base are the fire-places which open into the kiln. Except for hard porcelain the ware is fired twice, the first is called biscuit firing and requires the highest temperature and longest time. During this the body of the ware is solidified into a homogeneous mass and when withdrawn from the kiln it rings when struck almost like metal. The object of the second firing is to fuse and fix the glaze and is known as the "*glost*" firing. This requires less time and the temperature is not so high as in the first firing.

The decorations in design are fixed by a third firing which requires less time than either of the other two.

The porcelain industries in this country are centered at East Liverpool, Ohio, and at Trenton, New Jersey. The Rockwood potteries at Cincinnati are celebrated for their special ware, but it is a Fayence or porous ware. The Baltimore potteries also produce a porous ware, parian and majolica, the latter being quite celebrated. The common forms of pottery are produced at many other places in the United States.

Fire-ware. For the manufacture of fire-bricks and such articles of pottery as have to withstand a very high temperature it is of course necessary to employ infusible material. Nearly pure clay is used for these purposes to which is added a little sand or ground ware of the same description to prevent shrinkage. Crucibles are also made from clay mixed with an equal weight of graphite, such crucibles will withstand rapid changes of temperature with impunity.

Common bricks are made from less pure varieties of clay which contain sufficient fusible material to "clinker" the bricks during the burning.

EXPLOSIVES.

An explosion may in the most general sense be defined as a sudden and violent increase in the volume of a substance. In this general sense the increase may or may not be due to chemical transformations. This definition includes all action by which there may be violent increase of volume; thus a compressed gas or vapor is said to explode the action being mechanical and the result of the energy originally expended in bringing the gas to the compressed condition. In a more purely chemical sense an explosion may be defined as violent increase in the volume of a substance brought about by chemical transformation set up in it, resulting in large volumes of heated gases. A body capable of undergoing this sudden change by chemical transformation upon the application of the proper disturbing cause is an explosive.

For our purposes it will only be necessary to describe a few of the more important solid and liquid explosives.

In these explosives the energetic action is due to the rapid conversion of a solid or liquid into gases occupying many times the volume

of the original substance, the increased volume being due to the change of state and the expansion by heat, resulting from the chemical transformation of the explosive. It is evident therefore that the energy of the action of an explosive will depend largely upon the rapidity of the chemical transformation by which it is converted into gas and vapor. The heat of the transformation when the products are the same is independent of the time but the temperature is greater the shorter the time. In the useful explosives the heat liberated and the gases produced in the chemical transformation are mainly the result of oxidation processes, the bodies oxidized and the oxygen for the purpose all being present in the explosives themselves and the oxidation is independent of the oxygen of the air. The more important explosives all contain carbon as an essential element to be oxidized, other elements are also generally present. We may thus conceive explosions to be cases of a special kind of combustion. From a purely chemical view explosives can not be classified in a definite manner, but they may with some convenience and often are grouped into *explosive mixtures* and *explosive compounds*; these divisions are not entirely distinct nor accurate.

PREPARATION OF EXPLOSIVES.

EXPLOSIVE MIXTURES.

These consist of a mechanical mixture of two or more ingredients which upon the application of the proper disturbing cause undergo the transformation defined as an explosion.

Simple Explosive Compounds. These are definite chemical compounds which from the proper disturbing cause undergo explosion.

In such a compound the elements which enter the transformed products are all constituents of the single original body. In mixtures the elements so entering are constituents of the different composing ingredients.

These simple explosive compounds may be associated with other bodies simple or compound in such manner as to produce modified results in the explosion. The substances resulting from such association supply instances of explosives which might with equal propriety be put in either of the above classes. The great majority of the explosives however can be placed in one or the other group bearing in

mind the distinction that in explosive mixtures the ingredients are capable of mechanical separation and in such explosive compounds as contain more than one substance, they are not capable of separation by mechanical means.

Explosives are also sometimes classed as *high* and *low* explosives. The former term being applied to those explosives in which the transformation is so rapid as to produce a *rupturing* effect, the latter to those in which the transformation is less rapid and the effect, in general, one of *propulsion*.

Explosives are again sometimes classed as explosives of the *first* and *second order* depending upon the time involved in the transformation. In explosions of the first order the time is very short the action being practically instantaneous; in the second order the action is much slower the time being appreciable. Explosions of the first order are also termed *detonations*. Every explosive may be detonated and the order of the explosions graduate into each other. It is therefore evident that the classification just given (into high and low explosives and explosions of the first and second order) are without scientific basis and are not more distinctive than the divisions into explosive mixtures and explosive compounds. The terms, however, have a general significance and are convenient.

Explosive Mixtures. We have stated that an explosion may be considered as a combustion which is accomplished independently of the air and by the oxygen present in the explosive. In explosive mixtures one of the ingredients supplies the oxygen and the others the combustibles for oxidation. The most common oxidizing agents in explosive mixtures are the nitrates and chlorates. These salts form the basis for dividing the mixtures into the *nitrate* and *chlorate* mixtures. The former are the more important, the latter are however employed to a considerable extent in pyrotechny and in igniting other explosives.

Gunpowder. This substance is an intimate mixture of charcoal, sulphur, and nitre. For a satisfactory powder great attention must be paid to the purity of the ingredients. The source and general preparation of the ingredients have already been described. The proportions of the ingredients are usually taken as nitre 75 per cent, charcoal 15 per cent, and sulphur 10 per cent.

Nitre, KNO_3 . This is the oxidizing agent in gunpowder. The commercial nitre is always carefully refined before incorporation with the other ingredients. The great difference of solubility of nitre in hot and cold water is made use of in this refining. The impure salt is dissolved in hot water, the solution filtered to remove insoluble matter and allowed to cool under continual agitation. The nitre solidifies in minute crystals during the cooling and gives *saltpeter flour*. This flour is subjected to two or three washings in small quantities of water insufficient to dissolve it, to remove adhering liquid and then drained, when it is ready for incorporation.

The nitre for gunpowder should give no cloudiness in solution with a soluble salt of silver or of barium.

Sulphur. The crude sulphur of commerce is refined by distillation and the *distilled* sulphur is the variety used in the manufacture of gunpowder. It has been pointed out that the distilled sulphur belongs to the soluble or electro-negative variety while the sublimed sulphur belongs to the electro-positive variety. The first belongs to the same electro-chemical group as oxygen and it is conceivable that this fact may explain the difference in properties of the two varieties. It is generally thought that the sublimed sulphur from its mode of deposition may contain acid vapors in its interstices which would act detrimentally.

The sulphur for powder should burn without residue and water in which it has been steeped or agitated should not show distinct acid properties.

Sulphur lowers the igniting point of powder, accelerates

the combustion, increases the temperature of combustion, and the volume of gases evolved. It also gives permanent solidity to the grain and prevents crumbling to dust.

Charcoal. This is the principle combustible of the powder. By its oxidation are produced the gases carbon monoxide and carbon dioxide, with great evolution of heat. The charcoals employed result from the destructive distillation of several kinds of wood, all of which belong to the light woods as alder, dogwood, and willow.

The temperature at which the distillation is accomplished affects the quality of charcoal. The higher the temperature the more nearly pure the charcoal. In general it may be said that black charcoal results from temperatures above 340° C.; red from temperatures between 300° and 340° C.; and brown below 300° C.

The higher the temperature at which the charcoal is produced the less easily it ignites but the combustion is more rapid after ignition.

In some powders the percentage of the constituents is different from that given above. The cocoa powder contains more nitre and less sulphur. The Duponts in this country have made a brown powder in which the sulphur is less, the nitre more than that given, and a carbohydrate is used to replace some of the charcoal.

Many attempts have been made to replace potassium nitrate in black powder, but it has not been successfully accomplished. Sodium, ammonium, and barium nitrates have all been tried, but the first two are deliquescent and the last is too expensive. In the brown cocoa powder the carbon is obtained from rye straw.

The effects of powder when fired in guns depend both upon the composition and the physical texture and structure of the powder. These are all varied to meet the demands of the military service, and the discussion of these subjects does not pertain especially to chemistry.

Products from the Explosion of Gunpowder. The products from the explosion of powder vary with the conditions under which the explosion occurs. In general it may be said that the oxygen of the nitre combines with the carbon producing carbon monoxide and carbon dioxide. A part of the carbon dioxide combines with the potassium forming potassium carbonate. The sulphur is mainly converted into potassium sulphate. The nitrogen present in the powder is liberated. The nitrogen, the carbon monoxide, and the carbon dioxide expanded by the heat of the oxidation account for the explosive effect. The formula usually assumed to represent the general results of the explosion is $4\text{KNO}_3 + \text{C}_4 + \text{S} = \text{K}_2\text{CO}_3 + \text{K}_2\text{SO}_4 + \text{N}_4 + 2\text{CO}_2 + \text{CO}$.

Besides the products indicated there are always others present in small quantity. From the above formula by the consideration of molecular weights, it is seen that solids constitute nearly two-thirds by weight of the products of explosion and the gases a little over one-third. With brown, slow-burning powders the proportion of solids is less and that of gases more. The smoke from gunpowder is due to the solid constituents.

Gunpowder explodes at 316°C . It can be exploded by percussion.

Chlorate Mixtures. A large number of chlorate mixtures has been invented but none of them has found general application as powder. They are mainly used in pyrotechny and as fuse mixtures.

EXPLOSIVE COMPOUNDS.

It has already been stated that a simple explosive compound is composed of a single substance. Other explosive compounds are composed of more than one substance and while they are not definite chemical compounds their ingredients can not be separated by purely mechanical means as in the case of explosive mixtures.

The most important bodies which are classed as explosive compounds are the nitro-explosives or those explosives associated with other substances or with each other. In the nitro-explosives there is present as a constituent in the molecules an NO_2 group which supplies the oxygen involved in the chemical transformations of the explosive. This NO_2 group is introduced into the explosive by the action of nitric acid upon a hydrocarbon or a hydrocarbon derivative.

The most important of the nitro-explosives are the *nitro-compounds* and the *organic nitrates*. The most important group of the nitro-compounds are those resulting from the action of nitric acid upon the benzene hydrocarbons. Nitro-glycerine and gun-cotton are the most important examples of organic nitrates. Gun-cotton was formerly thought to be a nitro-substitution compound but it is now classed among the organic nitrates. Nitro-glycerine is an ethereal salt of nitric acid.

All these classes are produced by the action of nitric acid upon hydrocarbon derivatives and in each case the resulting molecular change consists in the substitution of one or more groups of NO_2 for one or more atoms of hydrogen in the derivative. The precise distinction between substitution compounds and organic salts will be stated after we have described some of the bodies. We may without any inconvenience consider the classes named as derived by the replacement of one or more hydrogen atoms by one or more groups of NO_2 . We shall first describe the two principal organic nitrates and some of their derivatives.

NITRO-GLYCERINE OR NITRIC GLYCERIDE.

Nitro-glycerine is prepared by the action of a mixture of strong nitric and sulphuric acids upon glycerine. The function of the sulphuric acid seems to be to preserve the strength of the nitric acid by combining with the water liberated during the transformation of the glycerine. The

reaction for the conversion is represented by $\text{C}_3\text{H}_5(\text{OH})_3 + 3\text{HNO}_3 = \text{C}_3\text{H}_5(\text{NO}_3)_3 + 3\text{H}_2\text{O}$. It is prepared by gradually adding glycerine to a mixture of strong nitric and sulphuric acids, the best proportions being three of nitric to five of sulphuric by weight, both acids being of great strength.

Properties of Nitro-glycerine. Nitro-glycerine is a heavy oily liquid of specific gravity 1.6 at 15°C . When pure it is white, without odor, but the commercial product is usually pale yellow. It is poisonous when taken internally. It is insoluble in water, soluble in ether, benzene and methyl-alcohol; it is less soluble in ethyl- than in methyl-alcohol. When pure it has been kept ten years without deterioration. It solidifies at about 8°C . though the freezing point varies with the quality of the nitro-glycerine. In the solid form it is much less sensitive than in the liquid state.

It explodes by concussion. If a small quantity of it be ignited it will burn away without explosion. In a confined space it explodes when heated up to 180°C ., though in small quantity it has been heated to a higher temperature without explosion. Nitro-glycerine which has not been thoroughly freed from acids or when subjected to too high a temperature is liable to become dangerous from spontaneous decomposition. It is exploded by detonation through mercuric fulminate. It will undergo the sympathetic detonation referred to by means of gun-cotton.

The products of the explosion of nitro-glycerine are shown by the reaction, $2\text{C}_3\text{H}_5(\text{NO}_3)_3 (\text{exploded}) = 5\text{H}_2\text{O} + 6\text{CO}_2 + \text{O} + 6\text{N}$. The temperature of combustion or calorific intensity of nitro-glycerine, that is the temperature to which its heat of combustion would raise the products, is 3005°C . according to Vuick. The gaseous products from the explosion of nitro-glycerine are about 1500 times the volume of the explosive taken at 15°C ., the gases being measured at the temperature of 100°C . and under atmospheric pressure.

Owing to the dangerous nature of liquid nitro-glycerine

its use in this form has long since been abandoned in Europe and it is now not generally used in this country.

Nitro-glycerine Derivatives. To overcome the objections to the fluid form many explosives of which this is the basis have been tried. These derivatives of nitro-glycerine may be grouped into two classes, 1st, When nitro-glycerine is associated with a chemically inert substance, and 2nd, When with a substance that takes chemical part in the explosion.

The most important of the first group is common dynamite, usually termed dynamite No. 1. It consists of nitro-glycerine absorbed by a porous siliceous earth which is mainly composed of the shells of diatomaceæ. The better forms of this earth will absorb three times their weights of nitro-glycerine. The earth only serves to give solid form to the explosive.

To the second class belongs a large number of explosives consisting of nitro-glycerine associated with chemically active substances. Charcoal and charred sawdust are used to absorb it and it is mixed with gunpowder and other nitrate and chlorate mixtures. Nitro-glycerine is also mixed with other nitro-explosives some of which will be mentioned later.

The objects aimed at in associating other substances with nitro-glycerine are to get it in less dangerous form than the liquid and at the same time to increase its effect by using as auxiliary substances bodies capable of combining with free oxygen seen to be present in the gases from the explosion of nitro-glycerine alone.

GUN-COTTON, PYROXYLIN.

This body is the nitrate of cellulose and results from the action of strong nitric acid upon cellulose. The NO_2 groups of the acid replace the corresponding number of hydrogen atoms in the cellulose. We have given the formula of cellulose as $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ which may be written $(\text{C}_6\text{H}_{10}\text{O}_5)_2$ or $\text{C}_{12}\text{H}_{20}\text{O}_{10}$. Using this formula the reaction for the production

of gun-cotton is $C_{12}H_{14}O_4(OH)_6 + 6(HO,NO_2) = C_{12}H_{14}O_4(O,NO_2)_6 + 6H_2O$. Gun-cotton is a hexanitate, six atoms of hydrogen being replaced by six NO_2 . The formula $C_{12}H_{14}O_4(O,NO_2)_6$ may be written $2C_6H_7O_5(NO_2)_3$, not forgetting its actual formula is a hexanitate; its production for convenience may be represented thus $C_6H_{10}O_5 + 3(HO,NO_2) = C_6H_7O_5(NO_2)_3 + 3H_2O$, making it similar to that for the production of nitro-glycerine.

Gun-cotton like nitro-glycerine is prepared by the action of a cold mixture of strong nitric acid and sulphuric acid upon cellulose. The sulphuric acid serves the same purpose as in the manufacture of nitro-glycerine. The cotton is perfectly freed from all grease and oil. It is next opened up by carding and cutting into short fibres. It is then ready for treatment with the acids, after which it has to be thoroughly washed to remove the acid. After washing, the cotton is now generally converted into a pulp by a machine similar to a rag-engine in a paper mill. It is then subjected to a final washing to remove every trace of the acid, drained and moulded into blocks, discs, and other forms that may be required. The gun-cotton is now seldom employed in the form of cotton wool.

From the chemical change indicated in the reaction it is seen that the cotton increases greatly in weight. In England from motives of economy, cotton waste is the material used for the conversion into gun-cotton.

Properties of Gun-cotton. Gun-cotton wool can not be distinguished from the raw cotton by the eye. It is harsher to the touch. It dissolves in acetic ether and acetone. If ignited when loose in the air, it flashes with a yellow flame. It can be exploded by a blow but generally only the particles struck explode. Fully nitrated cotton has often been heated rapidly to $180^\circ C$. without explosion but it is very risky to heat it above $175^\circ C$. and it often explodes below this.

Ignited in a confined space the burning of the first portion raises the remainder to the temperature of explosion. Either

the dry or wet cotton may be detonated by fulminate. Both nitro-glycerine and gun-cotton will undergo sympathetic detonation, that is, the detonation can be communicated along a row of cartridges of either of these explosives, though not in contact, when one of them is exploded. Gun-cotton like nitro-glycerine may be detonated under water.

The products of the explosion of gun-cotton vary somewhat with the conditions of the explosion but when perfectly detonated they may be expressed by the reaction $2\text{C}_6\text{H}_7\text{O}_5(\text{NO}_2)_3 = 7\text{H}_2\text{O} + 3\text{CO}_2 + 9\text{CO} + 6\text{N}$, which shows that it does not contain sufficient oxygen for the complete combustion of the carbon. All the products being gaseous as in nitro-glycerine there is no smoke. In mining operations the absence of smoke is advantageous but the effects of the carbon monoxide produced are detrimental. By associating the gun-cotton with some oxidizing agent the effect of the explosion may be increased and the carbon monoxide converted into carbon dioxide, thus for many purposes some nitrate is often associated with the gun-cotton.

Collodion Cotton; Soluble Pyroxylin. The common gun-cotton just described is a hexanitrate and is insoluble in a mixture of alcohol and ether. The collodion cotton is a mixture of several lower nitrates and is soluble in the alcohol and ether mixture. It is made by the action of weaker nitric and sulphuric acids upon the cotton. It is less explosive than gun-cotton but is largely manufactured for preparation of celluloid, smokeless powder, and gelatine explosives.

Gelatine Explosives. It has been seen that gun-cotton contains too little oxygen for the complete combustion of its carbon. As collodion cotton is composed of lower nitrates it contains still less in proportion to the carbon. The deficiency of the oxygen in the gun-cotton can be supplied by associating it with other substances and this is done in the gelatine explosives.

The simplest and one of the most important of the gelatine explosives is blasting gelatine. This consists of about seven parts of collodion cotton dissolved in about ninety-three parts of nitro-glycerine. The excess of oxygen in the latter supplies the deficiency of that element in the former. This explosive is more powerful than either of its constituents. Its sensitiveness may be increased by the addition of a little gun-cotton and decreased by the addition of a little camphor.

Blasting gelatine is an amber-colored soft elastic mass, which can be bent without permanently losing its shape.

Gelatine Dynamite. To diminish the violence of blasting gelatine, it is sometimes thickened with other ingredients, the nitro-glycerine in the gelatine being diminished. Gelatine dynamite and gelignite consist of the same ingredients as blasting gelatine in different proportions, incorporated with potassium nitrate and wood-pulp.

Celluloid. This substance is not classed as an explosive though masses of it have been known to explode. It is composed of collodion cotton and a large percentage of camphor. The proportions usually employed are two parts of collodion cotton and one part of camphor. Celluloid appears to be a mechanical mixture, the camphor being capable of extraction by proper solvents. Celluloid is generally made from tissue paper.

Xylonite and artificial ivory are forms of celluloid.

NITRO-EXPLOSIVES FROM THE BENZENE GROUP.

Nitro-compounds. As already stated the nitro-explosives from the benzene derivatives are nitro-substitution compounds as distinguished from organic nitrates. The distinction between the two classes will be referred to later, but as stated, for our purposes both classes may be assumed to be formed the same way, that is by the replacement of one or

more atoms of hydrogen in the hydrocarbon by one or more groups of NO_2 .

Nitro-compounds of Benzene. By the action of nitric acid upon benzene three nitro-benzenes may be produced, mono-, di-, and tri-nitro-benzenes, $\text{C}_6\text{H}_5\text{NO}_2$, $\text{C}_6\text{H}_4(\text{NO}_2)_2$, and $\text{C}_6\text{H}_3(\text{NO}_2)_3$. The first two are not explosive in themselves but are associated with other substances in the preparation of certain explosives. Tri-nitro-benzene is said to be explosive though it has not yet been used as such. The nitro-benzenes need not therefore be here considered as explosives. Mono-nitro-benzene is largely used to prepare aniline, from which is obtained a host of beautiful dyes.

Tri-nitro-phenol; Picric Acid. This is an important nitro-compound from the benzene derivative phenol. It is obtained by the nitration of phenol, carbolic acid, $\text{C}_6\text{H}_5\text{OH}$.

The action of nitric acid upon phenol may be represented by the equation, $\text{C}_6\text{H}_5\text{OH} + 3(\text{HO}, \text{NO}_2) = \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH} + 3\text{H}_2\text{O}$.

Picric acid is explosive and is used to a limited extent as such, but the acid is far more important because of the salts it produces which are more stable than the acid and very explosive.

It may be said that the nitro-compounds from the benzene group are not in general explosive and are not used alone but they are all used as auxiliaries in the preparation of explosives. It will only be possible to mention a few of the important examples.

Rack-a-Rock the explosive used in the great explosion at Flood Rock (Hell Gate), New York, consisted of mono-nitro-benzene absorbed by potassium chlorate.

Bellite. This is a mixture of ammonium nitrate and di-nitro-benzene.

Several military powders have been made which consist of mixtures of ammonium and potassium picrates with nitre or with nitre and charcoal.

Nitro-compounds and Organic Nitrates. The distinction between a nitro-compound or substitution product and a nitro-ether or ethereal

salt is based upon the transformations they undergo when subjected to the action of certain reagents. From this basis the NO_2 group which is present in both classes is believed to be differently attached in the molecule. Some of the nitro-compounds have the same molecular formulæ as certain nitro-ethers but they are found to be metameric bodies and not isomeric; thus the ether salt, $\text{C}_2\text{H}_5\text{ONO}$, (ethyl nitrite) is metameric with the substitution compound nitro-ethane $\text{C}_2\text{H}_5\text{NO}_2$. The reactions which the two classes undergo justify the belief that the hydrocarbon radical is connected to the nitroxyl group through the N atom in the substitution compound and through an O atom in the ethereal salt. There is also reason for thinking that the mode of formation of the two classes is different. This difference can be better understood by an illustration. The nitro-compound $\text{C}_6\text{H}_5\text{NO}_2$ (nitro-benzene) may be considered as produced by the action, $\text{C}_6\text{H}_5\cdot + \text{HONO}_2 = \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$, in which either the NO_2 replaces the H of the benzene or the C_6H_5 replaces the OH of the acid. Nitro-glycerine, the nitric ether of glycerine, is an ethereal salt of nitric acid resulting from the replacement of the hydrogen of the acid by the basic alcohol radical of glycerine, $\text{C}_3\text{H}_5(\text{OH})_3 + 3(\text{OH}, \text{NO}_2) = \text{C}_3\text{H}_5(\text{O}, \text{NO}_2)_3 + 3\text{H}_2\text{O}$. In this the trivalent radical C_3H_5 replaces three atoms of hydrogen, or the acid radical NO_2 replaces the hydroxyl hydrogen of the alcohol. Considering the hydrocarbon radical in the two cases, it is seen that in nitro-benzene the radical has replaced OH, in the nitro-glycerine it has replaced H. All ethereal salts may be considered as formed in this way, by the replacement of the hydrogen in the acid by the alcohol radicals.

These ethereal salts are also called esters and the distinction between the constitutional formulæ of these and nitro-compounds may be generally represented by $\text{R}-\text{NO}_2$ and $\text{R}-\text{O}-\text{NO}_2$, in which R stands for a hydrocarbon radical, the N atoms being directly connected with the radical in the compounds and through O atoms in the ethers.

Gun-cotton was formerly classed as a nitro-compound but it is now thought to be an organic nitrate, cellulose nitrate. This conclusion is reached from the fact that under the action of reagents its reduction products place it among the organic nitrates rather than among the nitro-substitution compounds.

SMOKELESS POWDERS.

It was natural that in the first efforts to prepare a smokeless powder as a propelling agent, it should have been attempted to use some of the known high explosives which left no solid residue in exploding. Many attempts were made to adapt gun-cotton to this purpose as it was thought to promise most favorable results. These early attempts were

all mainly based on a physical manipulation of the cotton wool and resulted in failure.

The smokeless powders of the present day may be grouped into three general classes. 1st, Those in which the only explosive used is some form of nitro-cotton; 2nd, Those in which nitro-glycerine and some form of nitro-cotton are used; 3rd, Those in which nitro-derivatives of benzene alone or with nitro-cellulose are used.

The more important and successful powders belong to the first class.

The first class includes a number of powders made by kneading the nitro-cotton in a proper solvent and bringing it to such a consistency that it can be rolled into tenaceous sheets after which it is cut into flakes. These powders are known as *flake powders* and are largely made in several European countries. By a little different manipulation the kneaded mass is converted into grains and gives *granulated powders*. The solvents used are acetic ethers or acetones. These powders sometimes contain some additional substance to retard their action when ignited, but by careful manipulation they are now made without such addition. The effect of the solvent and the physical treatment produce the desired result. Some of the powders are glazed which has a retarding effect upon their explosion. The second class includes a number of noted powders made by dissolving collodion cotton in nitro-glycerine or gun-cotton in nitro-glycerine and acetone.

In these powders the ingredients are kneaded or thoroughly mixed together and may be then rolled into sheets or cut into flakes or may be pressed through small cylindrical openings into cords or fibres. Ballistite, cordite, and the American Leonard and Peyton powders fall into this class. Each of these powders contains a small addition of certain other substances for decreasing rapidity of action.

The third class includes a number of powders resulting from associating picric acid or the picrates with other

substances, the picrates of potassium and ammonium are employed. In *indurite* invented by Professor Monroe formerly of the Naval Torpedo Station, gun-cotton is dissolved in nitro-benzene. One of the American smokeless powders by the Duponts is also made by dissolving nitro-cellulose in benzene. As already stated the last class is of little importance compared with the other two.

The number of explosives and powders is entirely too great to be here described or even mentioned. The physical manipulation involved in their preparation does not properly belong here and only their general chemical relations have been referred to.

FULMINATES.

The fulminates are the salts of fulminic acid. The acid has not been isolated but its formula is assumed to be $C_2N_2O_2H_2$. The principal salts of this acid are the fulminates of mercury and silver; the other metallic fulminates are obtained from these.

The most important is that of mercury commonly known as fulminating mercury. This fulminate is prepared by dissolving mercury in nitric acid and acting upon it with alcohol, its formula is $C_2N_2O_2Hg$.

It is a white solid when pure but is usually of a grey color. It is extremely sensitive to explosion and detonates by percussion, by heat ($187^\circ C.$), by the electric spark, or by contact with nitric or sulphuric acid. Its explosion is represented by the reaction $HgC_2N_2O_2$ (exploded) $= Hg + 2CO + N_2$.

It is used mainly to detonate other explosives. For this purpose it is employed either singly or with other substances. Potassium chlorate, nitrate, meal powder, and antimony sulphide are some of the common substances used with it.

The fulminate or the fulminating mixture is enclosed in thin metallic cylinders for use as detonators.

It will be observed that mercuric fulminate contains an NO_2 group and a hydrocarbon derivative (alcohol) is employed in its preparation though it does not contain hydrogen. The rational formula of the body has not yet been agreed upon.

ILLUMINATING GAS.

COAL GAS.

The idea of preparing an illuminating gas from coal seems to have become first well defined in the mind of

William Murdoch, a Scotchman, in 1792. In this year he lighted his house with coal gas. By the year 1800 he had extended the use of the new illuminant to all the principal shops and foundries near Birmingham. Murdoch's invention did not become known on the continent of Europe until the beginning of the nineteenth century. The French claim the invention for their countryman Lebon, who in 1801 illuminated his house with gas from wood. Gas lighting was first introduced into the streets of London in 1807 and had become general by 1814. Paris was lighted by gas in 1820 and after this date the use of gas rapidly spread over Europe. The manufacture of gas has ever since been an industry of great extent and magnitude. The gas generally designated as coal gas and used for illuminating purposes is a mechanical mixture of a number of permanent gases some of which are luminous while others produce little light when separately burned. There are also present the vapors of many substances which greatly add to the light-giving power of the gas. Coal gas is generally manufactured by the destructive distillation of bituminous coal.

Bituminous coal is essentially composed of carbon, hydrogen, oxygen, nitrogen, sulphur, and a little mineral matter. In general the carbon amounts to about seventy-five per cent of the coal. When bituminous coal is subjected to the action of heat out of contact with air, there results a large number of compounds composed of two or more elements of the coal. There have already been distinguished nearly a hundred bodies among the products of the distillation of coal. It is evident from this fact that coal is a complex body. The original arrangement of the elements in the coal has not been determined but it is certain that the numerous distillation products are not primary constituents of the coal but result from the application of heat. They are *products* of the distillation and not mere *educts* from the coal.

COAL GAS MANUFACTURE.

Retorts. In the manufacture, bituminous coal is placed in fire-clay retorts capable of being hermetically sealed. The retorts are generally D shaped cylinders about ten feet long and from fourteen to twenty inches in diameter. The charge of coal is usually from two hundred to four hundred pounds and remains in the retort from four to six hours. The coal is always introduced into a heated retort. The retorts are arranged in benches so that a number can be heated by the same furnace and they are kept above a red heat. During the heating the volatile products of the distillation are driven off and coke is left in the retorts.

The principal products of the distillation which pass from the retorts are vaporized liquid hydrocarbons, water vapor, hydrogen, marsh gas, acetylene, olefiant gas, ammonia, hydrogen sulphide, carbon dioxide, carbon monoxide, cyanogen, nitrogen, and carbon disulphide.

Ascension Pipe and Hydraulic Main. From the front upper surface of each retort rises an iron pipe. These pipes extend upward and then curve down and enter a large iron cylinder called the hydraulic main which runs perpendicular to and above the retorts and receives the pipes from all the retorts.

The hydraulic main is kept partially full of water and other condensed liquid-products of distillation. The ends of the pipes from the retorts dip beneath the liquid in the main. A portion of the heavy hydrocarbon vapors are condensed in the hydraulic main and nearly all of the aqueous vapor. The former constitutes tar and the condensed aqueous vapor takes up ammonia, carbon dioxide, hydrogen sulphide, and cyanogen forming what is known as the *ammoniacal liquor*.

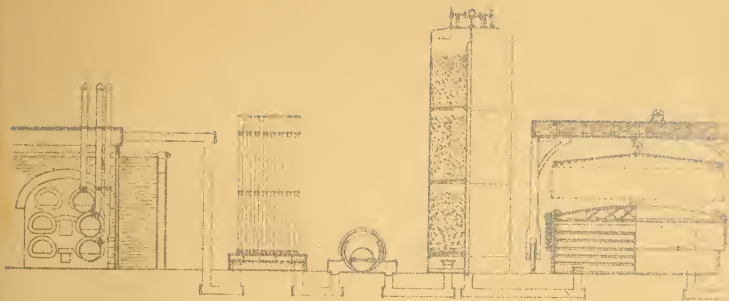
The gases and more volatile products of the distillation bubble up through the liquid in the main. This liquid acts as a seal to prevent the gases from returning to the ascension pipes when the retorts are open for recharging.

Condensers. From the hydraulic main the uncondensed products are carried by an iron pipe called the *foul main* to the condensers. The condensers are a series of pipes through which the gas passes and which furnish a large cooling surface; the condensers may be cooled by running water or simply by exposure to the air. In the condensers are deposited the liquid hydrocarbons (tar), ammoniacal salts, and aqueous vapor which have passed through the hydraulic main. The condensed products are conducted by pipes to suitable receptacles for removal.

Exhausters. Immediately after the condensers *exhausters* are usually placed. The exhauster is a form of pump for pulling the gas away from the retort and forcing it through the subsequent parts of the plant into the holder. If it were not for the exhauster the pressure of the gas in the retorts would have to be sufficient to overcome all the resistances in the different parts of the plant and thus cause loss of gas by leakage in the retorts.

Washers and Scrubbers. From the exhausters the gas passes through the washers and scrubbers or through scrubbers alone. The washers are arrangements in which the gas is made to traverse thin layers of liquid. In scrubbers the gas is not forced to pass through the water but is brought into intimate contact with wetted surfaces. A common form of scrubber is a cylinder filled with coke over which water continually trickles. In the passage through the washers and scrubbers the remaining ammonia and some of the hydrogen sulphide and carbon dioxide are removed.

Purifiers. From the scrubbers the gas passes through the purifiers, the object of which is to remove the remaining hydrogen sulphide from the gas. The purifiers are generally square iron boxes, divided by a number of horizontal sieves. The purifying material is placed in layers upon these sieves



and the gas is made to traverse the several layers before leaving the purifiers.

The materials used in the purifiers are slaked lime or iron oxide either separately or in succession. The slaked lime takes out both hydrogen sulphide and carbon dioxide while the iron oxide removes only the hydrogen sulphide. The carbon dioxide diminishes the illuminating power of the gas and when not removed the illuminating power can only be kept up by enriching the gas in a manner yet to be explained.

The great advantage of the iron oxide is that its purifying power can be restored a number of times by simply exposing it to the atmosphere. The lime can not be used again and can not be economically used except where it is very cheap and can be readily disposed of when spent. If the substances are used in succession it is better to pass the gas through the iron oxide first and then through the lime. When lime is employed as the purifying agent calcium sulphide and calcium carbonate are produced; when iron oxide is employed the mono- and sesqui-sulphides of iron are produced. When these sulphides are exposed to the air the iron oxide is reproduced and the sulphur deposited. The oxide may thus be repeatedly revived until the separated sulphur amounts to 55 per cent. Purification by iron oxide is the method now generally employed.

The reactions in the iron purifiers are $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} = 2\text{FeS} + \text{S} + 3\text{H}_2\text{O}$. The oxide is reproduced by exposure to the air and the reactions are $2\text{FeS} + \text{O}_3 = \text{Fe}_2\text{O}_3 + \text{S}_2$ and $\text{Fe}_2\text{S}_3 + \text{O}_3 = \text{Fe}_2\text{O}_3 + 3\text{S}$. The oxide of iron used may be a natural product, bog iron ore, or it may be artificially prepared by the oxidation of iron borings or filings. In this country the oxide is very generally prepared in the manner mentioned.

The carbon disulphide is one of the most difficult impurities to remove from the gas when it is there present, and

there is demanded for this result special provision not deemed necessary for description here.

The Gasometers. From the purifiers the gas passes to the holders or gasometers and is stored for use, and distributed as required to consumers.

The composition of purified coal gas differs at different places, in general it may be stated that the composition is approximately H=50 per cent: saturated hydrocarbons of the paraffin series mainly marsh gas=30 to 40 per cent; unsaturated hydrocarbons, mainly benzene, acetylene, and ethene, 3 to 5 per cent; nitrogen, 3 to 5 per cent; carbon monoxide, 3 to 5 per cent, with small quantities of oxygen and carbon dioxide.

The luminosity of the gas is believed to be due to the combined action of the hydrocarbons and can not in a great degree be attributed to any one of them alone. The quality of the gas is of course affected by the temperature of the distillation. At too low a temperature the solid and liquid hydrocarbons are too abundant, at too high a temperature the gaseous hydrocarbons are decomposed, carbon being deposited as gas carbon and hydrogen being liberated.

valley The illuminating power of gas from common coal was formerly ~~frequently~~ increased by adding to the charge of the retort a small quantity of cannel coal. This result is now frequently brought about by impregnating the gas with vapor of the volatile hydrocarbons. This is often done in this country by introducing into the retort a small iron cylinder (called cartridge) containing paraffin oil obtained from petroleum.

Secondary Products from Coal Gas Manufacture. The secondary products from the gas manufacture are numerous and important. The hydraulic main, the condensers, and the scrubber constitute the source of nearly all the ammoniacal salts of commerce. The coal tar by distillation

readily yields two portions, the light and heavy oil. From the light oil naphtha, benzine, toluene, and other less important bodies are obtained; from the heavy oil naphthalene and carboic acid are obtained. Besides the bodies named there are many others of great theoretical importance to organic chemistry.

ALCOHOLIC BEVERAGES.

The different alcoholic beverages of mankind may be grouped into two classes—1st, *fermented*, 2nd, *distilled*. The fermented may be divided into the less general classes, *beers* and *wines*. These classes with the general principles of their production will be briefly described.

Fermented Liquors; Beers and Wines. Beers are the products of fermentation of glucose which has been directly produced by the transformation of starchy substances. Wines are the products of the fermentation of glucose existing as such in the fruits used.

BEER-MAKING.

Malting. Beer is generally produced from barley. In the operation of malting, the grain is first soaked in water until it has swollen and become soft. It is then spread in layers, under the proper condition for germination, in a dark place kept at a constant and moderate temperature. Under these conditions the grain sprouts and when the radicle or sprout has grown to about half an inch, the vitality of the grain is destroyed by kiln-drying and the radicle made brittle by the final temperature, to which it is subjected, so that it is easily broken off and can be removed by sifting. The radicle is valuable as a manure as it contains about one-ninth the nitrogen of the grain.

During the germination the seed absorbs oxygen and gives off carbon dioxide and there is produced a substance known as *diastase* which converts some of the starch into

dextrin and glucose, which then serve as food for the developing radicle. Diastase contains carbon, hydrogen, oxygen and nitrogen but its formula is not known. The malted grain contains about one-fifth per cent of its weight of diastase.

Brewing. Preliminary to brewing the malted grain is ground to an even grist and infused in water at the temperature of about 77° C. when it is left for several hours, during which the diastase acts upon the unaltered starch and converts the greater portion of it into sugar and dextrin. The water with its dissolved constituents is called wort. It is drawn off from the exhausted malt and run into a wort-boiler. The exhausted malt contains some starch and nitrogenous matter and is used as food for animals.

The wort is next boiled with the requisite quantity of hops. The flowers of hops contain a bitter principle called *lupulin* and an essential oil. They confer upon the beer its aromatic flavor and odor and tend to prevent the conversion of the alcohol into acetic acid. The boiling also effects the removal of a considerable quantity of nitrogenous matter resulting from the gluten of the grain, which matter would be deleterious upon the keeping properties.

After boiling with the hops the wort is drawn off and cooled rapidly to about 15° C. to avoid the action of the air in producing acid fermentation, if cooled slowly. The wort is then transferred to the fermenting vessels or tuns and made to ferment by the addition of the proper quantity of yeast.

Yeast is a vegetable micro-organism (already referred to) which possesses the power of converting sugar into alcohol and carbon dioxide. It is also capable of inducing the conversion of cane sugar into glucose.

The fermentation is the most important part of the operation of brewing. The process is controlled by attention to the temperature of the liquid and the general appearance of

the tuns. The extent to which the fermentation has proceeded can be well determined by the density of the wort. The yeast is always removed before the fermentation is completed and the beer drawn off into casks where it undergoes a slow fermentation and then becomes charged with carbon dioxide.

The finished beer besides the water, alcohol and carbon dioxide, contains some unchanged glucose and dextrin, the extract from the hop, some nitrogenous matter from the grain, and the soluble mineral matter of the grain except the phosphates, which are consumed by the yeast. There are present in small quantity other secondary products of the fermentation as acetic acid, glycerin, etc.

Porter, stout, and highly colored beer are made by having a small quantity of the malt strongly dried or charred so as to convert some of the sugar into caramel. The amount of alcohol in beers varies from two to nine per cent.

The beer yeast if deprived of moisture by drying at a low temperature or by pressure can be kept for a long time without losing its powers but if heated to 100° C. it is killed and is no longer capable of producing fermentation.

The yeast plant grows and increases at the expense of the phosphates and nitrogenous matter of the wort, these being necessary to its growth. As previously stated it is during the growth of the yeast that fermentation takes place. In a solution of pure sugar the yeast will transform only a limited quantity of the sugar and is destroyed by the action.

WINE-MAKING.

We have stated that the wines result from the fermentation of the glucose existing in the fruits from which the wine is made. The term is generally applied only to those beverages made from grapes. Wine further differs from beer in that the maker adds no ferment. The expressed juice of the grape undergoes spontaneous fermentation. This fermentation is due to the fact that the yeast spores are gen-

erally present on the skin and stalks of the grape and are carried about by the air. The grape juice contains the necessary constituents for the sustenance of the yeast, and when the yeast spores are deposited in it they readily grow, with the resulting vinous fermentation. If all the sugar be fermented the wines are said to be dry, otherwise the wine remains sweet.

The skins, stalks, and seeds of the grape contain tannic acid with several coloring matters. The color and slightly astringent taste of the red wines are due to the fact that the skins are left for a certain time in the fermenting juice and the alcohol produced, dissolves out the tannic acid and the coloring matter. In white wine the fermentation does not take place in contact with the skins. Red wines are generally fermented in vats, white wines in casks.

After fermentation the wines are decanted and very frequently clarified in addition. Red wines are usually clarified by albumen, while the white are clarified by gelatin (isinglass). The action of the albumen or gelatin is purely mechanical. The tannin in the wine acts upon these bodies forming a precipitate which carries with it any suspended impurities of the wine. The great amount of tannin in the red wines permits the use of albumen, while isinglass is used with white wines.

Acid potassium tartrate is present in considerable quantity in the grape juice. The solubility of the salt decreases with the increase of alcohol so that the slight fermentation which goes on after the bottling or casking causes a deposition of the salt. With the removal of the tartrate the coloring matter becomes less soluble and falls giving the wine a lighter color.

In effervescent wines the fermentation is continued after bottling, and the carbon dioxide liberated under pressure, is retained in the liquid. Champagne is the most important effervescing wine. Its manufacture requires great care and

skill hence the wine is very expensive. For champagne the must or grape juice is very carefully clarified and the wine bottled before the fermentation has entirely ceased, sugar being added at the same time, as there is not enough left in the wine to continue the fermentation to the desired point. After fermenting for a time in the bottles the corks are removed and the compressed gas discharges the yeast and other impurities. The bottles are then refilled with a specially prepared white wine or liquor^w, recorked, and sealed for the market. The different processes require six or seven months and during the fermentation in the bottles there is much loss due to breakage. In the dryest champagnes the pressure of the gas often reaches five or six atmospheres.

In the manufacture of red wines it was formerly the custom in wine-making countries, and still is in some places, to crush the grapes by the bare feet of men treading upon them. This crushing is the preliminary to the pressing of the grapes. In the making of champagne the grapes are not crushed before being put into the presses, the only crushing being by the press; this gives a purer juice.

The reason that the grape is superior to all other fruits for wine-making is that its vegetable salt is potassium tartrate^{tr} which as above explained is deposited as the alcohol increases and the sugar disappears. Wine made from gooseberries, currants, apples, etc., contains malic and citric acids which can not be thus removed and consequently their acidity must be overcome by the addition of sugar.

Cider is a wine which results from the fermentation of the fruit sugar of the apple. It may contain from seven to ten per cent of alcohol.

A solution containing more than one-third its weight of sugar will not undergo vinous fermentation and when the alcohol produced amounts to about seventeen per cent of the solution the fermentation ceases. This limit fixes the maximum strength of fermented liquors.

DISTILLED LIQUORS.

The stronger alcoholic beverages of mankind result from the distillation of fermented liquors. They may be brought into two general classes, whiskies and brandies.

Brandies. These result from the distillation of wines. The brandy from ^{grape}wines is considered the best. In this country a brandy is made from apple cider and one from the juice of the peach.

Whiskey. Whiskey is made by distilling the fermented products of various starchy substances. Those generally used are Indian corn (maize), rye, barley, rice, and oats. In this country whiskey is made in large quantity, corn and rye being the principal grains employed. That from corn is generally known as *Bourbon whiskey*.

The grain is malted quite similarly as for beer, but as the diastase for the malt is far greater than necessary to convert its ^{starch}~~sugar~~ into ^{sugar}~~alcohol~~ distillers generally add a large portion of unmalted grain whose starch is also converted. The extract from the grain is fermented as in beer-making and as the distiller endeavors to produce as much alcohol as possible the fermentation is urged to its utmost. This fermented liquor is then subjected to distillation, the portion passing over during the process constituting the whiskey, the residuary liquid being of little value. The alcoholic strengths of both fermented and distilled liquors vary between wide limits and there is such a large number of each kind that it is impracticable to give detailed descriptions. The genuine wines, whiskies, and brandies are to a considerable extent now imitated by mixing liquors of different strengths and adding certain flavoring and coloring materials.

BREAD-MAKING.

The essential constituents of bread-making grains are water, starch, nitrogenous matter, dextrin, cellulose, a little

sugar and some fat, and inorganic salts. The nitrogenous matter is mainly in the form of gluten and albumin. The gluten is composed of vegetable fibrin, of a substance resembling casein and of vegetable gluten. The gluten is the most important constituent for bread-making. It is because of the tenacity of the wheat gluten that it is superior to all other grains for bread-making. This tenacity is due to the vegetable gluten or gliadin, it is this component of the gluten that gives adhesiveness to the dough.

When wheaten flour is kneaded upon cloth the gluten is left as an elastic, tenacious mass. The gluten is the main flesh-forming constituent of the flour, but in its natural state it is tough and difficult of digestion. In good bread the dough is so manipulated that the whole is rendered light and porous, thus becoming more palatable and more digestible, exposing a large surface to the action of the digestive fluids. Rye stands next to wheat as a bread-making grain, and it is largely used for that purpose in northern Europe. Wheat is the chief bread-making grain.

The essential and desired qualities of lightness and porosity are conferred upon bread by incorporating with the dough, carbon dioxide under pressure. The tenacity of the gluten prevents the ready escape of the gas and as it expands the required texture is produced in the dough. This vesiculated texture is made permanent in the bread by the solidification which results from baking.

The carbon dioxide employed may be produced by fermentation within the dough or is otherwise introduced therein. In the former case *fermented* bread results, in the latter *unfermented*.

Fermented Bread. In this kind of bread various kinds of yeast are employed, the result being a *vinous fermentation* by which the sugar of the dough is converted into carbon dioxide and alcohol. These escaping through the gluten cause the dough to *rise*. A little yeast incorporated with

some dough is placed in a suitable temperature. When this charge has *worked* a while it is kneaded with the remaining batch of dough. The fermentation then pervades the whole and after a short interval the loaves are formed and placed in the oven.

Sometimes leaven is employed to bring about fermentation. Leavening has been practiced from remote ages. It consists in placing a small quantity of dough under favorable conditions to undergo natural fermentation, and when this has set in, the leaven is mixed with the dough and the whole undergoes fermentation. In this case the cause of the fermentation is minute organisms introduced into the dough from the air.

In fermented bread the sugar which is fermented is that present in the grain and it is also partly derived from the conversion of starch into sugar. It is seen that *vinous fermentation* plays an important part in bread-making. A considerable amount of alcohol is given off in the making of such bread, and it acts like the carbon dioxide to lighten the bread. Efforts have been made to collect and save the alcohol given off in the manufacture of fermented bread, but the necessary arrangements injured the quality of the bread and were abandoned.

Unfermented Bread. The most direct method of preparing unfermented bread is illustrated in the making of aerated bread. In this process the flour is brought to the state of dough by kneading with water charged with carbon dioxide. The whole operation is mechanically performed in closed vessels. When the mixing is complete an opening is made at the lower part of the vessel and the dough is forced out by the pressure of the gas. The vesiculation is produced by the expansion of the gas, with which the dough is thoroughly impregnated. The expansion begins when the dough is removed from the vessel and is still further increased by the heat of the oven. In this process

the dough and bread are untouched by the hands of the baker until removed from the oven.

Unfermented bread is also made by the use of certain powders, which react upon each other when moistened with water and liberate carbon dioxide. The most common of these is a mixture of tartaric acid and acid sodium carbonate. If the powders be thoroughly incorporated with the flour the gas will be liberated during the kneading with water. Another method is to mix the sodium carbonate with the flour and then knead with slightly acidulated water; dilute hydrochloric acid is frequently employed. Ammonium carbonate is sometimes used, it being volatile at the temperature of baking.

Flour is injured if it becomes damp or moist, its gluten becoming somewhat soluble and less tenaceous. Such flour is greatly improved by adding to the water used in making the dough, lime water in the proportion of twenty-seven pints to one hundred pounds of flour.

Hard Bread. This kind of bread is made by baking the prepared dough without vesiculating material of any sort. All the moisture is expelled from such bread and it is much more dense than soft bread and keeps far better. It is accordingly better for military and naval stores. Other grains than wheat and rye can be used for making hard bread.

One hundred pounds of flour will make considerably over one hundred pounds of soft bread, depending upon the proportion of the crust and this depends upon the size of the loaves. Ordinarily the weight of soft bread will exceed the weight of flour by about one-third. The weight of hard bread is less by about one-seventh. The staleness of bread is not due to its becoming dry, as is frequently supposed, but results from molecular change. Its freshness can be restored by rebaking in a closed oven.

The cereal grains are richer in inorganic salts and fatty

matter in and near the husk. As there is frequently some of the integument carried away with the husk, it is evident that unbolted flour has some superiority over the bolted. If bread supplied the only article of food this difference between the flours would be more important. Besides the physical condition of bread which makes it more palatable and more digestible than dough, other important changes are brought about by the baking. The state of nitrogenous constituents is altered and made more digestible. The starch granules are ruptured and some of it transformed into dextrin and sugar both of which are soluble: this latter effect is especially noticeable in the crust and in toast.

THE PREPARATION OF SOAP.

A fuller account of the fats and fixed oils, than has yet been given, will lead to a better understanding of the chemical principles of soap-making.

Fixed Oils; Fats; Glycerides. These are terms applied to a large number of analogous bodies found in both plants and animals. It is an interesting fact that there should be such a striking resemblance in composition and properties between bodies from such distinct sources.

The term *fixed oils* is generally used for those members of the group which are liquid at ordinary temperature and the term *fats* for those that are solid. A fat is a solid fixed oil.

These bodies are ethereal salts of the fatty acids. The basic part of the salt is the alcohol radical C_3H_5 . They are all capable of saponification yielding glycerine and a fatty acid. Owing to the above facts the class is very properly termed *glycerides*. Some of the characteristics of the glycerides are as follows.

Composition. They are all composed of carbon, hydrogen and oxygen, being very rich in hydrogen and carbon. They yield glycerine and a fatty acid by saponification.

Solubility. They are practically insoluble in water, but dissolve in ether, carbon disulphide and mix in all proportions with essential oils.

Stability. If the air be excluded they can be preserved for a long time. In contact with air some of them absorb oxygen and in thin layers become solid. Such of the fixed oils are called *drying oils*. This oxidation may take place with considerable elevation of temperature. If the oil expose a large surface, as when tow or cotton waste is moistened with it, spontaneous combustion may result. Other of the fixed oils when exposed to the air do not dry up but become rancid and ropy. This change is attributed to the presence of impurities. Such oils are called *non-drying*. The fixed oils cannot be distilled without decomposition. They are unctious to the touch and the more liquid leave a permanent stain on paper.

Some of the more important of these oils and fats are the following: Palm, cocoa-nut, castor oil, cotton-seed and olive or sweet oil. Hemp, poppy oil and linseed oil are drying oils, the last named being much used by painters. Its drying powers are increased when it is boiled with certain metallic oxides. Such oxides are termed *siccatives*. The oils just named are of vegetable origin. Some of the others ordinarily obtained from animal sources are stearin, Palmitin, margarin and olein. Butter is mainly composed of Palmitin, stearin and olein. Bees-wax is a fat.

It will be seen that the above characters establish a broad distinction between the fixed oils and the essential or volatile oils.

MANUFACTURE OF SOAP.

Soap manufacture is an ancient and important industry. The remains of a complete soap-making establishment were found in the excavations of Pompeii, with soap still perfect though made over seventeen hundred years ago.

It has just been stated that the more important vegetable and animal fats and oils are composed of a fatty acid in

which the hydrogen is replaced by C_3H_5 , the radical of glycerine or propenyl alcohol, the oils and fats being glycerides. The general significance of the term *saponification* has been given. Soap is here used in the ordinary sense.

The natural fats or glycerides may be represented by the formula $C_3H_5Ft_3$, in which (Ft) stands for a complex molecule of carbon, hydrogen and oxygen. The fatty acid from which the glyceride is derived would be represented by FtH . A soap may be defined as the salt of a fatty acid in which the hydrogen has been replaced by an alkali metal.

Soaps are made by the action of an alkali upon the glycerides (fats) or sometimes upon fatty acids. The alkalies employed are potassa and soda. The action is brought about by boiling the fat with the caustic solution and may be indicated by the reaction $C_3H_5(Ft)_3 + 3NaOH = 3NaFt + C_3H_5O_3$,
Soda Soap
Glycerine

or potassium hydroxide may be used instead of sodium hydroxide with the resulting production of a potash soap. It will be observed that the alkali metal has replaced the basic radical C_3H_5 . Soaps are generally stearates, oleates or palmitates of potassium and sodium.

Soaps containing sodium are generally hard and those containing potassium are generally soft, though it is possible to produce a soft soda soap and a hard potassium soap. The soaps of the alkali metals are soluble, those of other metals generally insoluble.

Soap can be produced from a large number of fats and oils, but only a comparatively small number is employed. The principal animal fats are tallow, suet, lard, whale, seal and fish oils; the vegetable oils commonly used are palm, olive, cocoa-nut and cotton seed. Fish oils contain a large proportion of olein, a liquid fat, and are generally used with potash to form soft soap, especially in Europe. In this country the farmers, in the south and south-west, frequently make soap for domestic use from kitchen fats and the alkali obtained from wood-ashes.

The alkali used is generally in the form of the hydroxide when soaps are made from fats. Certain soaps are made by boiling the alkaline carbonates with free fatty acids obtained in other operations. The alkaline hydroxides are prepared in enormous quantity for use in soap-making.

The glycerine formed during saponification may or may not be separated from the soap. Castile soap is made from olive oil and marine soap from palm oil. Soap may contain from 25 to 75 per cent of water. In the high dry regions of our western country soaps have been known to lose nearly one-half their weight by evaporation of water.

The subsequent treatment of the soap after removal from the boiling vessels depends upon the object desired and is very varied. Many different kinds of ingredients are incorporated for the purpose of affecting the color, odor and other properties of the soap.

Cleansing Power of Soap. This property of soap is largely due to its alkalinity. Even a neutral soap gives an alkaline solution when treated with water, some of the alkali separating and leaving a soap with a greater amount of fatty acid than previously existed. The excess of alkali acts upon the grease or other insoluble matter and often renders its removal possible. To increase the detergent power of soap substances are often added which act merely mechanically, such are sand and silicate of soda.

MANUFACTURE OF LEATHER.

The antiquity of this industry is unknown, but it is certain that it was practiced by the ancient Egyptians, for pieces of leather taken from a mummy and now in the British Museum, bear marks showing that it must have been made 900 years B.C. It is well known that the Romans attained much skill in the preparation and finishing of leather and it is thought that the Chinese were acquainted with the art from remote ages. On the other hand it is

strange, when we recall how universally the skins of animals are used by savages, that so many of them should have remained ignorant of the art of tanning almost up to the present time.

Leather. If the fresh skin of an animal, cleaned and divested of hair, fat and other extraneous matter, be immersed in a dilute solution of tannic acid a chemical combination ensues and the gelatinous tissue of the skin is converted into a non-putrescible substance, impervious to and insoluble in water. This is *leather*.

TANNING.

Preparation of Hides; Cleansing. The first step in the preparation of leather is the softening and cleaning of the hides. This is done by soaking in water, with frequent changes, until the skins are pliable. They are then put through a kneading process. The length of time that the hides must be soaked depends upon the manner of their original curing. The hides from hot dry countries sometimes require two or three weeks' soaking.

Depilation. The hair is removed from the cleaned skins by soaking them in lime water; the lime saponifies the fat around the roots of the hair and loosens them; or the same result may be accomplished by what is termed *sweating*. In this process the hides are suspended in pits and kept at a uniform temperature (18° C.) and a moist atmosphere until they undergo partial decomposition. The ammonia produced acts in the same way as the lime. The sweating process is almost exclusively followed in this country in the treatment of dried hides. The time necessary in this operation varies with the character of the hides treated so that no particular statement applies.

After the hair is scraped off the hides are treated for the removal of lime when this substance has been used as a

depilatory. This is generally done by steeping in a dilute solution of sulphuric acid. In this country hides for heavy leather are generally subjected to acid treatment though the sweating process has been employed. The acid, if properly used, exerts a beneficial action in preparing the skin for tanning. The acid is said to *plump* the fiber. The skins for sole leather are generally colored during the plumping. In leathers which are required to be soft it is found necessary to remove the lime by treating the hide with some putrefactive or fermenting *bate*. This softens the hide by its action on the fibrous tissue and *abates* plumpness. Such *bates* are sour bran, hen's or pigeon's dung.

Conversion Into Leather. In this country the tanning materials used are almost exclusively oak and hemlock barks. The greater part is tanned by hemlock. The bark is first thoroughly ground and then leached to extract the tanning principle from it. The bark liquors are then run into the vats, where the hides are packed. The hides are successively transferred to vats in which the liquor is stronger. In many American tanneries the process is completed in from sixty to seventy-five days from the time the hides are first subjected to the action of the liquors.

In England and America the tanning materials are generally leached or exhausted and the aqueous extract or decoction used in the tanning vats. The operation of tanning is thus shortened.

On the continent of Europe and at many places in this country after the hides are subjected to a weak infusion of the bark, they are packed in pits with alternate layers of bark; the pit is filled with water and the whole left for two or three months. The hides are then removed and treated in the same way in another pit with fresh bark, the order of the hides in the pit being reversed at each transfer. By this method the tanning often requires from ten to fifteen months. During tanning the hide increases in weight from 30 to 40 per

cent. The above description applies to the common heavier leathers. Many different tanning materials are used in different countries and a great variety of leathers produced, of these it is here practicable to refer to only a few of the more common forms.

Morocco. The genuine original morocco was made from goat skins, but it is now said that an equally good article is made from the skin of the hairy seal. Imitation morocco is made from sheep-skins. For morocco the depilation is by lime and the lime is removed by *bate* (pigeon's dung). The skins are tanned by extract of sumach. They are sewed into bags, filled with the tanning liquid and floated in a tank of the same. The process is usually complete in twenty-four hours. Morocco is generally colored after the tanning and the aniline dyes are largely used for this purpose.

Russian Leather. This form of leather is tanned with willow or larch bark. It owes its peculiar odor to the essential oil of birch-tar with which it is treated after tanning. Many imitations of this leather are now made.

Tawing. Kid. The leather for kid gloves is made from the skin of goats and lambs. The skins are unhaired by lime and the ~~hair~~^{lime} removed by sour bran. The tanning is accomplished by agitating the skins in a drum containing a mixture of flour, alum, salt and yolk of eggs. The aluminum chloride produced prevents putrefaction of the skin and the oil and albuminous matters increase softness and pliability. This process is called *tawing*. The kid is colored after tawing.

Buckskin; Chamois Leather. These leathers are made from the skins of goats, sheep and deer. The skins are prepared, limed and *bated* in the same manner as for morocco. They are then thoroughly impregnated with fish, whale or other oils by repeated steeping and drying. All

the water of the hides is thus removed and its place taken by oil. The skins are then exposed to a warm atmosphere during which some of the oil oxidizes and the skins take a yellow color. The excess of oil is then removed by an alkaline solution. It is not thought that any chemical change occurs in the skin itself, but the fibers are coated by the oily products and are very permanent and will not yield gelatine with boiling water. Kid does yield gelatine. Thicker hides than those above named may be used for this leather, but in that case they are made thin by splitting and rejecting the grain side.

Animal Parchment. This parchment is made by the mechanical treatment of lamb and goat or other thin skins after the hair is removed in the usual way. The skins are stretched on frames and rubbed to the necessary thickness by sand or pumice stone.

It is now possible to imitate very closely the natural grain of any leather. The thickness desired can also be secured, for the modern splitting machines have succeeded in splitting a common cow-hide into three and even four layers. By these means all the fancy kinds of leather can be imitated. Split leather is not so lasting as the natural skin of the same thickness, but it is cheaper. The splitting is best done before tanning. The skins from which leathers are made are those of the ox, horse, sheep, goat, pig, seal, deer and kangaroo.

PREPARATION OF CHEESE.

For the better understanding of the process of cheese-making it will be well to specify the composition of milk. The milk of all animals, both carnivorous and herbivorous, contains about the same constituents, though the proportions of the constituents vary considerably.

Milk consists essentially of water slightly alkaline, in which are dissolved casein, milk sugar and inorganic salts, and in which float numerous fatty globules. The fatty matter is the source of butter.

Good fresh milk is alkaline, its alkalinity is due to soda, which holds the casein in solution. If left to itself it soon becomes acid, from

the formation of lactic acid through the fermentation of the milk sugar. Milk is admirably adapted to the nourishment of the animal frame.

CHEESE.

Cheese is made by coagulating the milk by the addition of *rennet*, which is part of the stomach of the calf. A piece of rennet is added to a large quantity of milk, which is then slowly heated to about 50° C. In a short time after this temperature is reached the milk separates into a white coagulum or *curd*, and a slightly yellow translucent liquid called *whey*. The curd contains the casein of the milk, much of the fat and some of the inorganic salts. The whey contains the sugar, some of the fat and the remainder of the inorganic salts.

The curd is separated from the whey, well kneaded with some common salt and often some coloring substance is added. It is then pressed in moulds and set away in an airy and cool place to *ripen*. During the ripening the cheese undergoes a peculiar putrefactive fermentation, not well understood, by which it acquires its characteristic taste and odor. The changes during ripening are brought about by the decomposition of the casein and probably of some of the fat.

The quality of the cheese, of course, depends upon the kind of milk employed and the extent to which the ripening is carried. The amount of fat largely determines the quality of the cheese, the best qualities containing considerable fat, while the poorer are made from skimmed milk. The vesicular appearance of certain kinds of cheese is caused by the imperfect removal of the whey from the curd. The sugar of the whey ferments during the ripening, producing alcohol and carbon dioxide: these expanding produce the vesicles. Cheese with less fatty matter keeps better than richer cheese.

From the constituents of cheese it is evident that it possesses considerable dietetic value. In many places it is an important article of daily diet. Cheese can be made from the milk of any animal, but generally comes from the milk of the cow; it is a product of many countries. It is largely made in this country and of excellent quality. The curd can be separated by adding a little acid to the milk and heating, but this is seldom done in cheese-making.

The successful preparation of artificial butter (oleo-margarine) has led, in some places, to the use of this substance for the fatty principle of cheese, thereby permitting the use of skimmed milk. It is reported that this is done to a considerable extent in this country and that cotton-seed oil is also here used for the same purpose.

The red and blue moulds which grow upon cheese are vegetable fungi. The *cheese maggot* and the *cheese mite* are animal organisms. Cheese like meat may and has been known to undergo decomposition with the development of poisonous properties.

DYEING.

Dyeing is the art of imparting color to various substances, usually textile fabrics, in such manner that it is permanent under the conditions to which the fabric is subjected. In dyeing the color penetrates the material dyed, which is not the case in painting.

In order that the dye may penetrate the fabric it is evident that the former must be in solution. It is often only necessary to steep the fabric in a solution of the coloring matter, the attraction between the two imparting a permanent color. In the absence of the necessary attraction between the fabric and the dye-stuff, a third substance is employed which has an attraction for both; such substances are called mordants. When mordants are used there are usually two steps in the operation of dyeing—first, the application of the mordant; second, of the coloring matter. The nature of the action between the fabric and the mordant and between the fabric and the dye when mordants are not used, is not clearly understood. The facts and evidence at present seem to indicate that in some cases the action is physical and in others that it is chemical.

In cotton, linen and vegetable substances generally, the action seems to be more of a physical one than in the case of silk, wool and other animal substances. As a general fact the coloring material permeates the latter class more fully than the former, and they may be dyed with greater facility and more permanently—the vegetable substances more frequently require mordants. The action between the mordant and the dye is in most cases a chemical one.

Mordants. The mordants can generally be classed as acid or basic. The principal mordant of the first class is tannic acid. Other vegetable acid principles and fatty acids are used for the same purpose. The basic mordants comprise a number of metallic salts, the principal of which are salts of aluminum, iron, chromium and tin.

The processes of mordanting cloth are too numerous even for present mention. The fibers of the cloth are impregnated with the mordanting substance in soluble form and by subsequent treatment it is rendered insoluble, if not naturally so after its union with the fiber. Usually mordanting precedes dyeing, but sometimes the operations are simultaneous and occasionally the dyeing precedes the mordanting.

Dyestuffs. The chemical character of many of the numerous dyestuffs classes them as either basic or acid. Each of them requires to be combined with a mordant of the opposite character to yield a dye.

We may illustrate the mordanting action by a simple case. If cotton be steeped in a solution of tannic acid it will absorb it; if it is then dipped into a basic coloring matter the acid combines with it and the fiber is dyed. Again, if cotton be steeped in a solution of aluminum acetate and then boiled, a basic acetate is deposited in the fiber. If the

cotton be now dipped into the solution of an acid coloring principle it will be permanently dyed.

Printing. If the dye be applied to only parts of the cloth, so as to produce patterns it is called printing. In goods requiring mordants this is easily accomplished by mordanting only those parts to be printed. Sometimes the cloth is uniformly dyed and the pattern effect produced by removing the color from certain parts. This can be done by bleaching agents and is known as the *discharge* method.

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